SOME ASPECTS OF THE ORGANOMETALLIC CHEMISTRY OF GALLIUM AND INDIUM

by

NICHOLAS CHARLES BLACKER

A Thesis submitted as part requirement for the
Degree of Doctor of Philosophy

University of Warwick
Department of Chemistry

August 1992

CONTENTS

		Page
CHAPTER 1	Introduction. Gallium and Indium	1
I.	Gallium and Indium	2
II.	Trivalent Organometallic Chemistry of the Group 13 Elements	4
II.1.	Oligomerisation	5
II.2.	Group Exchange	5
II.3.	Neutral Adduct Formation	6
II.4.	Formation of Anionic Complexes	10
II.5.	Alkane Elimination Reactions	10
II.6.	R_2M^+ Cations	13
II.7.	Reaction with Oxygen	14
II.8.	Insertion Reactions	15
III.	The Organometallic Chemistry of Gallium and Indium	18
III.1.	The Preparation of Simple Trialkyl, Triaryls and Organometallic Halides	18
	A. The Trialkyls and Triaryls	18
	B. The Organometallic Halides	21
III.2.	Functionalised Organometallic Compounds	23
III.3.	Neutral Adducts	23
III.4.	Reactions of R_3M with Acids	27
	A. Metal-Carbon Bonds	28
	B. Metal-Nitrogen, Metal-Phosphorus and Metal-Arsenic Bonds	29
	C. Metal-Group 16 Bonds	34
	(I) Hydroxides, Alkoxides, Aryloxides and Related Species	34

Page

III.4. C. (ii) Organometallic Carboxylates and Thiocarboxylates 35
(iii) Other Metal-Oxygen Bonded Compounds 37
D. Compounds Containing Metal-Nitrogen and Metal-Oxygen Bonds 37
E. Miscellaneous Compounds 38

CHAPTER 2 A Study of Organogallium-Amidine Complexes 39
Introduction 40
Preparation of Dimethylgallium-Amidine Complexes 41
Some Aspects of the Chemical Reactivity of the Complexes 43
Spectroscopic Properties of the Dimethylgallium-Amidine Complexes 48
X-Ray Crystallographic Studies 62

CHAPTER 3 Two New Organogallium-Macrocycle Complexes 73
Introduction 74
Preparation of the Complexes 76
Spectroscopic Properties 79
X-Ray Crystallographic Studies 85

Page

CHAPTER 4	**Some Co-ordination Compounds of Dimethylindium Iodide**	99
	Introduction	100
	Preparation of the Complexes	102
	Spectroscopic Properties	103
	X-Ray Crystallographic Results	110
CHAPTER 5	**An Examination of Three New Potential Methods for the Production of Gallium and Indium Trialkyls.**	116
	Introduction	117
	Reaction of Lead Tetraalkyls with Gallium and Indium Metals	117
	The Reaction between Gallium, Sodium and Ethyl Halides	119
	Exchange Reactions between Gallium(III) and Indium(III) Chlorides and Tetramethyl- and Tetraethyllead	119
APPENDIX A	**The Use of Quantitative N.M.R. Experiments to Investigate the Hydrolysis of Two Organoindium Iodides**	127
APPENDIX B	**The Preparation of $Br_3In_2(CH_2CO_2Et)_3$**	131
APPENDIX C	**X-Ray Crystallographic Studies**	134

		Page
APPENDIX D	**Experimental**	158
	General Experimental	159
	Chapter 2	160
	Chapter 3	169
	Chapter 4	172
APPENDIX E	**Mass Spectra**	176
REFERENCES		208

Page

FIGURES AND TABLES

CHAPTER 1.

Table 1.	Some physical properties of gallium and indium	2
Figure 1.	MX_3 monomer and bridging dimer	4

CHAPTER 2.

Table 1.	Some examples of pseudo-allyl ligands	40
Table 2.	New dimethylgallium-amidine complexes prepared during this study	42
Table 3.	Summary of T.G.A. results	46
Figure 1.	^1H N.M.R. spectra of N,N′-diphenylbenzamidine and dimethylgallium-N,N′-diphenylbenzamidine	49
Figure 2.	^1H N.M.R. spectra of N,N′-di(p-chlorophenyl) acetamidine and dimethylgallium-N,N′-di(p-chloro-phenyl)acetamidine	50
Table 4.	^{13}C N.M.R. results for some dimethylgallium-amidine complexes	52
Table 5.	The differences between the I.R. spectra of the amidines and the dimethylgallium complexes	54
Figure 3.	Fragmentation scheme for mass spectrum of dimethylgallium-N,N′-diphenylbenzamidine	57
Figure 4.	Fragmentation scheme for mass spectrum of dimethylgallium-N,N′-diphenylacetamidine	58
Figure 5.	Fragmentation scheme for mass spectrum of dimethylgallium-N,N′-di(p-chlorophenyl) acetamidine	59

Page

Figure 6.	Fragmentation scheme for mass spectrum of dimethylgallium-N,N′-diphenylformamidine	60
Figure 7.	The molecular structure of dimethylgallium-N,N′-diphenylbenzamidine, as determined by a single crystal X-ray diffraction study	63
Figure 8.	Another view of the molecular structure of dimethylgallium-N,N′-diphenylbenzamidine	64
Figure 9.	Comparison of the principal bond lengths in N,N′-diphenylbenzamidine and dimethylgallium-N,N′-diphenylbenzamidine	66
Figure 10.	Comparison of the principal bond angles in N,N′-diphenylbenzamidine and dimethylgallium-N,N′-diphenylbenzamidine	67
Figure 11.	Comparison of the principal bond lengths of dimethylgallium-N,N′-dimethylacetamidine dimer and bis(dimethylgallium)-N,N′,N″,N‴-tetramethyl-oxamidine	69
Figure 12.	Comparisons of the principal bond angles in dimethylacetamidine dimer and bis(dimethylgallium)-N,N′,N″,N‴-tetramethyloxamidine	70
Table 6.	Gallium-carbon and gallium-nitrogen bond lengths in dimethylgallium-amidine complexes.	72

CHAPTER 3

Table 1.	Published organogallium-macrocycle complexes	74
Figure 1.	Molecular structures of reported organogallium-macrocycle complexes	75

		Page
Figure 2.	Combined T.G.A. and D.T.A. plot for $Me_2GaHtmtaa$	77
Table 2.	Summary of ^1H N.M.R. data for H_2tmtaa, $Me_2GaHtmtaa$ and MeGatmtaa	79
Figure 3.	^1H N.M.R. spectra of MeGatmtaa, $Me_2GaHtmtaa$ and H_2tmtaa	80
Figure 4.	^{13}C N.M.R. spectra of MeGatmtaa, $Me_2GaHtmtaa$ and H_2tmtaa	81
Table 3.	Summary of ^{13}C N.M.R. data for H_2tmtaa, $Me_2GaHtmtaa$ and MeGatmtaa	82
Table 4.	Summary of the E.I. mass spectra of H_2tmtaa, $Me_2GaHtmtaa$ and MeGatmtaa	84
Figure 5.	The molecular structures of H_2tmtaa, $Me_2GaHtmtaa$, MeGatmtaa, showing bond lengths	86
Figure 6.	The molecular structure of $Me_2GaHtmtaa$ showing atom numbering scheme	87
Figure 7.	Another view of the structure of $Me_2GaHtmtaa$ illustrating the pronounced saddle shape of the ligand	88
Figure 8.	The molecular structure of MeGatmtaa, showing the atom numbering scheme	89
Figure 9.	Another view of the structure of MeGatmtaa, again showing the saddle shape of the ligand	90
Figure 10.	Side view of the neutral ligand, H_2tmtaa, showing its saddle shape	92

Page

Table 5.	C-N-C bond angles in H_2tmtaa, Me_2GaHtmtaa and MeGatmtaa	93
Table 6.	Significant bond angles at gallium in Me_2GaHtmtaa and MeGatmtaa	94
Figure 11.	The co-ordination geometry of gallium in Me_2GaHtmtaa and MeGatmtaa	95
Figure 12.	The co-ordination geometry of the dimethyl-gallium unit in $Me_2Ga(C_{12}H_{25}N_2O_4)(GaMe_3)_2$	96
Table 7.	Important bond lengths in organogallium-macrocycle complexes	97

CHAPTER 4.

Table 1.	Neutral co-ordination compounds of the organoindium halides	101
Table 2.	Ligands reacted with dimethylindium iodide	102
Table 3.	^1H N.M.R. data for the dimethylindium iodide adducts and parent ligands in $CDCl_3$	104
Table 4.	^{31}P N.M.R. data for the dimethylindium iodide adducts and parent ligands in C_7H_8/C_7D_8	104
Table 5.	Major indium containing fragments from the E.I. mass spectrum of Me_2InI.TMEDA	106
Table 6.	Major indium containing fragments from the E.I. mass spectrum of $Me_2InI.PPh_3$	106
Table 7.	Major indium containing fragments from the E.I. mass spectrum ofMe_2InI.DPPM	107
Table 8.	Major indium containing fragments from the E.I. mass spectrum of Me_2InI.diphos	107

Page

Table 9.	Major indium containing fragments from the E.I. mass spectrum of $Me_2InI.AsPh_3$	107
Table 10.	The differences between the I.R. spectra of the dimethylindium iodide adducts and free ligands.	109
Figure 1.	The molecular structure of $Me_2InI.TMEDA$	111
Figure 2.	Another view of the structure of $Me_2InI.TMEDA$	112
Figure 3.	The molecular structures of $Me_2InI.TMEDA$ and $EtInI_2.TMEDA$	113
Table 11.	Bond lengths in $Me_2InI.TMEDA$ and $EtInI_2.TMEDA$	
Table 12.	Bond angles in $Me_2InI.TMEDA$ and $EtInI_2.TMEDA$	114

CHAPTER 5.

Table 1.	^1H N.M.R. spectra of the organometallic chloride mixtures	122
Table 2.	^{13}C N.M.R. of the organometallic chloride mixtures	123
Table 3.	Summary of ^1H and ^{13}C N.M.R. spectra of Me_3PbCl and Et_3PbCl	124
Table 4.	Unassigned bands in the I.R. spectra of the products of the reaction between PbR_4 (R = Me, Et) and gallium and indium trichlorides	126

APPENDIX A

Table 1.	The results of the quantitative N.M.R. experiments	129

		Page
Table 2.	^{1}H and ^{13}C N.M.R. chemical shifts of hydrolysed $Me_3In_2I_3$	130
APPENDIX C		
Table 1.	Bond lengths for dimethylgallium-N,N′-diphenyl-benzamidine	141
Table 2.	Bond angles for dimethylgallium-N,N′-diphenyl-benzamidine	141
Table 3.	Atomic co-ordinates for dimethylgallium-N,N′-diphenylbenzamidine	142
Figure 1.	Molecular structure of N,N′-di(p-tolyl)benzamidine	144
Table 4.	Bond lengths for N,N′-di(p-tolyl)benzamidine	145
Table 5.	Bond angles for N,N′-di(p-tolyl)benzamidine	146
Table 6.	Atomic co-ordinates for N,N′-di(p-tolyl)benzamidine	147
Table 7.	Bond lengths for $Me_2Ga(C_{22}H_{23}N_4)$	149
Table 8.	Bond angles for $Me_2Ga(C_{22}H_{23}N_4)$	149
Table 9.	Atomic co-ordinates for $Me_2Ga(C_{22}H_{23}N_4)$	150
Figure 2.	The unit cell of $MeGa(C_{22}H_{22}N_4)$	152
Figure 3.	The orientation of one molecule in the unit cell of $MeGa(C_{22}H_{22}N_4)$	153
Table 10.	Bond lengths for $MeGa(C_{22}H_{22}N_4)$	154
Table 11.	Bond angles for $MeGa(C_{22}H_{22}N_4)$	154
Table 12.	Atomic co-ordinates for $MeGa(C_{22}H_{22}N_4)$	155
Table 13.	Bond lengths for $Me_2InI.TMEDA$	157
Table 14.	Bond angles for $Me_2InI.TMEDA$	157
Table 15.	Atomic co-ordinates for $Me_2InI.TMEDA$	157

Page

APPENDIX D

Figure 1.	Calibrated cold finger device used for measuring out liquid trimethylgallium.	162
Table 1.	Infra-red data for the dimethylgallium-amidine complexes and gallium(III)chloride-N,N′-di (p-chlorophenyl)acetamidine	168
Table 2.	Summary of infra-red spectra of H_2tmtaa, Me_2GaHtmtaa and MeGatmtaa	171
Figure 2.	Method used to grow crystals of Me_2InI.TMEDA	174
Table 3.	Summary of the infra-red spectra of the dimethylindium iodide adducts	175

ACKNOWLEDGMENTS

The author would like to thank the following people for their help during the course of this work:-

Professor M G H Wallbridge for his help and guidance throughout.

Dr J Barker of the Associated Octel Company for his assistance, encouragement and free lunches.

Dr N W Alcock and **Dr W Errington** for carrying out the X-ray crystal structure determinations, detailed herein.

Dr O W Howarth, J Lall and **J Hastings** for running many of the N.M.R. spectra reported in this work.

Mr I K Katyal for his help by obtaining most of the mass spectra used in this thesis.

All of the technicians in the Chemistry Department at the University of Warwick and the Analytical Department at Octel for their invaluable assistance.

A special thanks to **Mrs M S Callaway** for her efforts in typing this thesis.

The Associated Octel Company and the S.E.R.C. for providing finance for this work.

DECLARATION

All of the work described in this thesis is original and was, except where otherwise indicated, carried out by the author.

Nicholas C Blacker
August 1992

Some of the work described in Chapter 3 of this thesis has been published in the following reference:

N.W. Alcock, N.C. Blacker, M.G.H. Wallbridge and J. Barker, *J. Organomet. Chem.*, 1991, **419**, C23.

SUMMARY

This thesis describes a broad study covering several aspects of the organometallic chemistry of gallium and indium.

A study has been performed on the dimethylgallium-amidine complexes formed by elimination of CH_4 from mixtures of trimethylgallium and amidines. Some data have been obtained on their thermal decomposition reactions in view of their potential use as "III-V" semiconductor precursors. An X-ray crystallographic study was carried out on dimethylgallium-N,N′-diphenylbenzamidine. It was found to be monomeric, with the ligand chelating, in contrast to the only previously reported dimethylgallium derivative of a simple amidine, that of N,N′-dimethylacetamidine, which is dimeric with bridging ligands.

Two new organogallium aza-macrocycle complexes have been prepared using an unsaturated ligand 5,7,12,14-tetramethyldibenzo [b,i][1,4,8,11] tetraazacyclotetradecine ("H_2tmtaa"). The molecular structure of both compounds has been determined by X-ray crystallography. In the dimethylgallium compound the molecule is asymmetric with the gallium atom in a tetrahedral environment co-ordinated to two nitrogen atoms on one side of the macrocyclic ring. On heating, the monomethylgallium compound is produced. This provides an uncommon example of gallium in a square based pyramidal co-ordination environment, the gallium atom positioned above the centre of the N_4 ring.

Work was also carried out on the co-ordination chemistry of dimethylindium iodide with ligands containing Group 15 donors, particularly phosphorus, as there is a sparsity of literature covering this area. Unfortunately, no crystal structure data were obtained on compounds with phosphorus or arsenic-based ligands, but the structure of the dimethylindium iodide-TMEDA complex was determined.

Minor studies were also conducted on a potentially simple preparation of the trimethyl- and triethyl-derivatives of gallium and indium, including exchange reactions between gallium and indium trichlorides and lead tetralkyls. The stability of monomethyl and dimethyl-indium species in aqueous solution has also been investigated briefly by a quantitative N.M.R. method.

ABBREVIATIONS

TMEDA	Tetramethylethylenediamine
N.M.R.	Nuclear Magnetic Resonance
R,R′	Alkyl group
Me	Methyl
Et	Ethyl
n-Pr	n-Propyl
i-Pr	i-Propyl
n-Bu	n-Butyl
i-Bu	i-Butyl
s-Bu	s-Butyl
t-Bu	t-Butyl
Ar	Aryl
Ph	Phenyl
Cp	Cyclopentadienyl
M,M′	Metal
X	Halide
L,L′	Ligand
N.Q.R.	Nuclear Quadrupole Resonance
bipy	2,2′-bipyridine
nap	Napthyl
diphos	*bis*-1,2-diphenylphosphinoethane
triphos	*bis*(2-diphenylphosphinoethyl)phenylphosphine
tetraphos	*bis*-1,2-[(2-diphenylphosphinoethyl) phenylphosphino]ethane
DPPM	*bis*-1,1-diphenylphosphinomethane
phen	1,10-phenanthroline
dpt	1,3-diphenytriazene
T.M.S.	Tetramethylsilane

p.p.m.	Parts per million
T.G.A.	Thermogravimetric Analysis
D.T.A.	Differential Thermal Analysis
M.W.	Molecular Weight
H.C.B.D.	Hexachlorobutadiene
I.R.	Infra-Red
U.V.	Ultra-Violet
Vis	Visible
E.I.	Electron Impact Ionisation
C.I.	Chemical Ionisation
F.A.B.	Fast Atom Bombardment
H_2tmtaa	5,7,12,14-tetramethyldibenzo [b,i][1,4,8,11]tetraazacyclotetradecine
cyclam	1,5,8,12-tetraazacyclotetradecane
v/v	volume/volume
g.c.m.s.	Gas chromatography mass spectrometry
D.M.S.O.	Dimethylsulphoxide
acac	acetylacetone
F.T.	Fourier Transform
C.W.	Continuous Wave
I.T.D.	Ion Trap Detection
vs	Very strong
s	Strong
m	Medium
w	Weak
vw	Very weak
sh	Shoulder
br	Broad
str	Stretch

CHAPTER 1

Introduction

CHAPTER 1. Introduction

I. Gallium and Indium

Gallium and indium are Group 13 elements, lying between aluminium and thallium in the Periodic Table. Some of the physical properties of the free metals are tabulated below.[1]

Table 1. Some physical properties of gallium and indium

Property	Gallium	Indium
Atomic number	31	49
Atomic weight	69.723	114.82
Common isotopes (% abundance)	^{69}Ga (60.4%)	^{113}In (4.3%)
	^{71}Ga (39.6%)	^{115}In (95.7%)
Electronic configuration	Ar, $3d^{10}$, $4s^2$, $4p^1$	Kr,$4d^{10}$, $5s^25p^1$
Specific gravity (temp°C)	5.907 (solid, 29.6°)	7.30 (20°)
	6.095 (liquid, 29.8°)	
Melting point (°C)	29.78	156.61
Boiling point (°C)	2403	2080

Note - gallium has one of the largest liquid ranges of any known metal.

Both are rare and expensive elements, obtained as by-products during the extraction of other elements. The limited supply ensured that, until quite recently, the chemistry of gallium and indium was little investigated, especially in comparison with the large amount of work done on boron and aluminium. Since the discovery of two new, high technology applications, however, they have become more readily available and the subject of much increased levels of research activity. Interest in the

aqueous solution chemistry of the M(III) ions has been stimulated not only by the need for better extraction processes, but also because of their use in medical imaging. Work on their organometallic chemistry is largely stimulated by the continuing search for improved methods for the production of the "III-V" semiconductor materials, particularly gallium arsenide and indium phosphide. However, despite this recent work, many gaps in our knowledge remain. This thesis describes research carried out to investigate three areas of the organometallic chemistry of gallium and indium, as described below. Firstly, reactions of trimethylgallium with amidine ligands, and a study of the co-ordination compounds formed following the elimination of methane. Secondly, interactions of trimethylgallium and macrocyclic ligands containing NH groups, and finally, the co-ordination chemistry of dimethylindium iodide, with particular emphasis on compounds containing organophosphorus ligands. Minor studies have also been conducted on a potentially simple preparation of the trimethyl- and triethyl- derivatives of gallium and indium, including exchange reactions between gallium and indium trichlorides and lead tetraalkyls.

The remainder of this introduction will be devoted to a concise review of the organometallic chemistry of Group 13, and begins with a brief guide to the main reaction types which illustrate the trends down the group. It is followed by a more detailed discussion of the known gallium and indium compounds, with particular emphasis on the areas relevant to the work reported later. Work published prior to 1982 has been well covered in a review by Tuck[2a].

II. The Trivalent Organometallic Chemistry of the Group 13 Elements

The Group 13 elements have the ground state valence shell electron configuration ns^2np^1 (where n = 2-6 for boron - thallium). As a result, their chemistry is primarily that of the +3 oxidation state. Organometallic compounds with a formal oxidation state of +2 and +1 do exist (e.g. $[(i\text{-}C_4H_9)_2Al]_2$ [3] and CpIn [4]), but these are relatively few in number and will not be discussed here.

Compounds of the general formula MX_3 would be expected to have trigonal planar geometry (sp^2) with an empty p orbital perpendicular to the MX_3 plane, as shown below (Figure 1a)

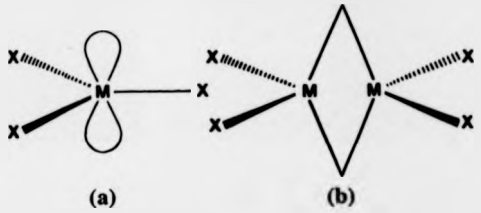


Figure 1 MX_3 monomer (a) and bridging dimer (b)

Because the metal centre is two electrons short of a stable "octet" such compounds would be expected to be electron acceptors - indeed they are sometimes said to be "electron deficient" which although strictly incorrect, is nevertheless a convenient way to describe their tendency to attain the eight valence electron arrangement whenever possible. In the following section it can be seen that the chemistry of the Group 13 trialkyls and organometallic halides is dominated by their Lewis acid properties. This and the other main features of their chemistry are outlined below. The examples quoted will often refer to boron or

aluminium compounds since it is for these elements that the most data are available.

1. Oligomerisation

One method of reducing electron deficiency is by oligomerisation (Figure 1b). The straight chain aluminium trialkyls, up to $(n\text{-}Bu)_3Al$ are predominantly dimeric in benzene solution[5-8], but the branched chain alkyls are monomeric due to steric hindrance. The physical properties of the aluminium trialkyls have been tabulated by Eisch[2b]. In contrast, even the trimethyl derivatives of boron,[2c] gallium, indium[2a,6,9] and thallium[2d] are monomeric in solution at room temperature and in the liquid states.

Most of the organometallic halides R_2MX and RMX_2, are dimeric, with halogen atoms in the bridging position, though there are exceptions. For example, the dialkyl fluorides often form higher oligomers - in benzene Et_2AlF is tetrameric[10] and R_2GaF (R = Me, Et) are trimeric[11], while some derivatives are ionic, such as $MeInI_2$ which has the structure $[Me_2In]^+[InI_4]^-$ in the solid state.[12,13] The physical properties of the organoaluminium halides have been summarised (by Eisch[2b]) as have the crystallographic data for the equivalent gallium and indium compounds.[2a]

2. Group Exchange

The presence of the empty p-orbital provides an obvious route for group exchange reactions and these are commonly facile. These redistribution reactions can occur between two triorgano species (Equation 1) and between a triorgano species and another trivalent species, most commonly the trihalides (Equation 2).

$$R_3M + R_3'M \rightleftharpoons R_2MR' + RMR_2' \qquad (1)$$

$$R_3M + X_3M \rightleftharpoons R_2MX + RMX_2 \qquad (2)$$

It has been postulated that exchange occurs via a bridged (dimer-type) transition state, even for predominantly monomeric compounds.[14-18] Strong evidence for this comes from the very slow rate of exchange of boron trialkyls in the absence of traces of boron hydride species or aluminium trialkyls.[19]

For the aluminium compounds it is suggested that the thermodynamic driving force behind such redistribution reactions to favour asymmetrical products is to maximise the number of bridging positions occupied by strong bridging groups.[2b] The bridging ability of alkyl groups is related inversely to their bulkiness, although despite their size, unsaturated groups preferentially occupy these positions unless hydride or other yet stronger bridging groups (e.g. halogen) are present.[2b]

For redistribution reactions to be a useful method for obtaining pure products usually requires this bridging priority effect to operate, as in the reaction below.[20]

$$2Ph_3Al + 1/n[AlH_3]_n \longrightarrow 3Ph_2AlH$$

Alternatively, the reaction can be driven to completion if one product can be removed, as in the thermal disproportionation of methylaluminium sesquiiodide, $Me_3Al_2I_3$, to give trimethylaluminium.[5] Redistribution reactions can also occur between two different metal centres. The use of this type of reaction in the preparation of gallium and indium trialkyls will be discussed later.

3. Neutral Adduct Formation

In principle any Lewis base should form an adduct with these compounds. Numerous examples exist for all members of Group 13. However, the stoichiometry of the adducts varies considerably and is not

always easy to predict. Most common are adducts with a 1:1 donor:acceptor ratio and tetrahedral geometry, but for the larger metals, especially indium and thallium, 2:1 and 3:1 adducts are well known, particularly when the metal is present as a relatively strong acceptor species such as an organometallic halide. These five and six co-ordinate species typically display trigonal bipyramidal and octahedral geometries, respectively.

The complexes vary greatly in stability - for the process:-

$$R_3M + L \rightleftharpoons R_3M.L \qquad (M = B, Al, Ga, In, Tl)$$

at ambient temperature the position of the equilibrium may lie in either direction. A number of methods have been used to establish orders of both donor and acceptor strength, for simple R_3M compounds with a wide range of donors, particularly from Groups 15 and 16 of the Periodic Table, although further work would still be of value. In 1956, Coates and Whitcombe published an order of acceptor strength of the trimethyl-derivatives, B < Al > Ga > In > Tl (with Ga > B) based mainly on gas phase heats of dissociation.[21] Subsequent work, outlined below, mostly confirms this general trend including the variable position of boron, especially with respect to indium and thallium, although it has been noted that some weak donors will co-ordinate to Me_3Ga, but not Me_3Al, presumably because of the activation energy required to split the Me_6Al_2 dimer.[22] By similar methods, the Lewis acidity of the triphenyl derivatives towards pyridine was found to fall in the order Al > Ga > B > In.[23]

Measurements of the dipole moments of both the triphenyl and triethyl compounds in dioxane show the following gradation Al > Ga > In > Tl > B.[24,25] Observation of changes in the asymmetric C ≡ O

stretch of dicarbonyl (cyano) π-cyclopentadienyliron which occur upon co-ordination with a Lewis acid lead to the proposal of a partial order $Me_3Al > Me_3B \approx Me_3Ga$.[26] A study of Pt-H nuclear magnetic resonance (N.M.R.) coupling constants of Lewis acid adducts of cyano (hydrido)bis(triethylphosphine)platinum, $H(Et_3P)_2PtCN$, give a ranking $Ar_3B > R_3B > Ar_3Al > R_3Al$.[27] This last study indicates that Lewis acidity of R_3M is, not surprisingly, affected to some extent by the nature of the R group. Earlier thermochemical measurements[23,28] suggest that Lewis acidity decreases in the series

$$Ph_3Ga > Me_3Ga \approx (vinyl)_3Ga > Et_3Ga$$

implying that the greater electronegativity of the unsaturated groups outweighs the effect of any conjugation and, where applicable, steric effects. Substitution of successive organic groups by halides would be expected to cause increased Lewis acidity, and this has been shown to be the case by complexation with alkali metal chlorides[29] and by N.M.R. studies.[30] Interestingly, it has been shown for the diethylaluminium halides that acceptor strength increases in order $F < Cl < Br < I$[31] which agrees with the acceptor strength of the trihalides being $Cl < Br < I$ (AlF_3 is ionic) a similar order to that of boron (although the effect is smaller), reflecting decreased bridging strength $Al_2I_6 < Al_2Br_6 < Al_2Cl_6$.[32] The trihalides of gallium and indium show reversed ("normal") acceptor strengths i.e. $Cl > Br > I$ (although again the effect is small) and it would be interesting to know if this is true for the organometallic halides.[32-35]

Donor strength varies much as would be expected, except for some anomalies due to steric effects, particularly for boron compounds. The complexation of trimethylaluminium by a number of Group 15 and 16 methyl derivatives has been studied, both qualitatively (by displacement reactions) and quantitatively.[7,36,37] For the reaction:-

$$\underset{(\text{monomer,gas})}{Me_3Al} + \underset{(\text{gas})}{L} \rightleftharpoons \underset{(\text{gas})}{Me_3Al.L}$$

the heats of reaction have been determined and the following order of donor ability established:-

$$NMe_3 > PMe_3 > OMe_2 > SMe_2 > SeMe_2 > TeMe_2$$

For trimethylgallium the sequence has been found to be[37].

$$Me_3N > Me_3P > Me_2O > Me_3As > Me_2Se >$$
$$Me_2S \approx Me_2Te > Me_3Sb > Me_3Bi$$

It can be seen that, unlike with Me_3Al, the dimethyl derivatives of sulphur, selenium and tellurium do not follow the expected order. A more recent study[38] gives the order $Me_2S \geq Me_2Te > Me_2Se$. It is clear that work remains to be done in this area, especially using other alkyl and aryl groups and halides. Again, other techniques have been used. N.M.R. methods have been used to produce a relative order of base strengths for triethylgallium[39]

$$MeNH_2 > NH_3 > NHMe_2 > NMe_3 > PMe_3 > OMe_2 > SMe_2$$

which, for the nitrogen derivatives, illustrates the importance of steric effects. With trimethylaluminium, ^{27}Al nuclear quadrupole resonance (N.Q.R.) measurements give an order of donor strength[40]:-

$$Me_3Sb < Me_2S < Me_3As < Me_3P < Me_3N.$$

4. Formation of Anionic Complexes

This may be seen as a special case of (3). Reactions of the type:-

$$L_3M + M'L' \longrightarrow M'.ML_3L'$$

occur for all members of the group and again they are normally carried out by simply mixing the two compounds in an appropriate solvent. L and L′ are usually alkyl, aryl halide or pseudohalide groups, in numerous combinations, but apparently no mixed complexes of the type $M'^{+}[MR_nR'_{4-n}]^{-}$ or $M'^{+}[MR_n(X,Y)_{4-n}]^{-}$ have been prepared.[2a] M′ is usually a Group 1 metal ion, or R_4N^{+}, although the structure $[Me_2In]^{+}[InI_4]^{-}$ was noted in Section 1.[12] Representative examples include the well known $NaBPh_4$, $K[Et_2AlCl_2]$[29] $[Me_4N]$ $[(Et_3Ga)_2F]$,[41] $[n\text{-}Pr_4N][CpInI_3]$,[42] $[Me_4N][Me_2Ga(N_3)_2]$,[43] $Li[Me_3GaH]$[44] and $[Me_4N][Me_3TlCN]$[45]

5. Alkane Elimination Reactions

As is typical of organometallic compounds, the Group 13 trialkyls and triaryls are reactive towards Brönsted acids (and occasionally other active hydrogen atoms). It is believed that the initial step is normally co-ordination to form an adduct, followed by the elimination reaction:-

$$R_3M + AH \longrightarrow R_3M.LA \longrightarrow R_2MA + RH\uparrow$$

In some cases, such as the reaction of Me_3Ga and Ph_2NH, below, the adduct has been isolated and characterised but in others (e.g. hydrolysis reactions) it has not.

The 1:1 reactions between Me_3M (M = Al, Ga, In) and Ph_2ZH (Z = N, P, As) have been investigated in detail.[46] Methane elimination occurs at temperatures between 0°C and 170°C. With trimethylaluminium the order of reactivity, (as indicated by decreasing temperature at which the reaction occurs) is N > P > As, in line with greater donor strength and electronegativity. For Me_3Ga and Me_3In this sequence is reversed.

Another very important aspect of this reaction is the number of metal alkyl groups removed, and the ease with which this occurs. The hydrolysis reaction is probably the best illustration of this, and the reaction has been relatively well studied for all of the Group 13 elements. Trimethylboron is unreactive to water at room temperature[47] but heating with one equivalent of water for seven hours at 180°C produces a 69% yield of dimethylborinic acid (Me_2BOH). The trialkylboranes are also surprisingly resistant to mineral acids and only one alkyl group was removed from $(n\text{-}Bu)_3B$ by refluxing with 48% hydrobromic acid for 1h.[48] They are, however, much more susceptible to attack by carboxylic acids, and under appropriate conditions, one, two or all three alkyl groups may be removed.[49-51] Steric effects are also important - secondary alkyl groups react more slowly[51] and tertiary even more so.[52] Vinylboranes are more reactive[53] as is Ph_3B.[54]

R_3Al compounds are much more reactive and protic solvents readily cleave all three Al-C bonds.[55] The gallium trialkyls are intermediate in their activity. They can react explosively with water but

under controlled conditions only one alkyl group is lost at room temperature, even with excess water.[55,57,58] Another is lost slowly at about 60°C[58] and reaction of Ph_3Ga is complete after 24 hours in warm, dilute sulphuric acid.[59] Trimethylindium is believed to evolve two moles of methane on reaction with cold water or methanol[60] and a third with dilute acids. Et_3In, however, only loses one alkyl group in cold water but all three at 90°C. Ethanol, even at 70°C, liberates only one mole of ethane.[61] In view of this, the reaction of Me_3In is surprising, especially as the dimethylindium cation, Me_2In^+ has been shown to be stable in aqueous solution (see Section (6) below). Quantitative N.M.R. experiments suggest that all three methyl groups of $Me_3In_2I_3$ survive on hydrolysis (this thesis, Appendix A). Me_3Tl and Et_3Tl again, only lose one alkyl group in water.[62,63] The stability of diarylthallium derivatives is well illustrated by the following reactions[64]

$$2PhB(OH)_2 + TlCl_3 + 2H_2O \longrightarrow Ph_2TlCl + 2B(OH)_3 + 2HCl$$

$$2PhTlBr_2 \xrightarrow{H_2O} Ph_2TlBr + TlBr_3$$

$CH_3CO_2TlEt_2$ and $CH_3CO_2TlPh_2$ are known to be stable to excess acetic acid.[65]

As a general rule, therefore, gallium, indium and thallium trialkyls only lose one mole of alkane with protic reagents under mild conditions.

Alkane elimination reactions involving the organometallic halides have been the subject of little study. The reactivity of carbon aluminium bonds is illustrated by the reactions below:-

$$n\ MeNH_2AlEt_2Cl \xrightarrow{75°C} (MeNHAlEtCl)_n + nC_2H_6\uparrow$$

$$(MeNHAlEtCl)_n \xrightarrow{215°C} (MeNAlCl)_n + nC_2H_6\uparrow$$

$$MeNH_3Cl + Et_2AlCl \xrightarrow{0°C} MeNH_2AlEtCl_2 + C_2H_6\uparrow$$

No HCl was evolved and the adducts react rapidly with moisture.[66] Similarly, Me_2AlCl reacts with methanol to form Me(Cl)AlOMe. Equivalent gallium and indium species would be expected to react less readily, and it is not clear from the available literature how the compounds Me(Cl)GaOMe and $Me(Cl)GaO_2CMe$ were prepared.[67,68] Secondary phosphine adducts of alkylgallium and indium halides will, however, eliminate alkane (rather than hydrogen halide) at 100 - 200°C.[69,70]

$$Me_2InI.HPBu^t_2 \longrightarrow 1/n[Me(I)InPBu^t_2]_n + CH_4\uparrow$$

6. **R_2M^+ Cations**

Water stable R_2M^+ species have been prepared for all members of Group 13 except aluminium.

Diphenylbipyridylboronium chloride may be prepared in 50-55% yield by boiling diphenylborinic acid or its ethanolamine ester with bipyridyl and 5M hydrochloric acid for 2-3h.

$$Ph_2BOH + bipy + HCl \longrightarrow (Ph_2B,bipy)Cl + H_2O$$

This ion is decomposed by aqueous base. Metathetical reactions yield other salts, such as the nitrate and perchlorate.[71]

Me_2GaOH, prepared by the hydrolysis of Me_3Ga, dissolves in nitric and perchloric acids, and addition of NaOD to the solutions precipitates Me_2GaOD. The cation (Me_2Ga^+) is believed to have a bent C_{2v} structure, with two co-ordinated water molecules.[72] The reaction of R_3M with anhydrous sulphuric acid in a 2:1 ratio leads to dialkyl-metal sulphates, $(R_2M)_2SO_4$ (R = Me, Et; M = Ga, In, Tl). These also dissociate in aqueous solution.[73] Vibrational spectra taken after hydrolysis of Me_2InO_3SMe have shown that Me_2In^+ is also C_{2v}[74] and is

probably *cis*-$[Me_2In(H_2O)_4]^+$.[2a] Diorganothallium compounds form a weakly solvated linear cation in oxygen donor solvents.[75]

Vibrational spectra have been used to infer the presence of Me_2In^+ in the solid state structure $[Me_2In]^+[InI_4]^-$[12,13] but X-ray crystallographic studies have been performed on a number of ionic diorgano thallium compounds. In Me_2TlCl the Me_2Tl unit is linear, and, in addition, each thallium is surrounded by four chlorine atoms to give octahedral co-ordination overall.[76] In dimethylthallium phenanthroline perchlorate the C-Tl-C angle is 168.3° despite the presence of the phenanthroline.[77]

7. Reaction with Oxygen

The reactivity of these compounds towards oxygen follows a similar sequence to hydrolysis. The most important exception to this is the pyrophoric nature of the boron trialkyls, in contrast to their inactivity with water. Controlled oxidation typically produces $RB(OR)_2$ species,[78-80] but in the presence of water R_2BOR is formed.[79] A number of reactivity series have been summarised by Odom.[2c] Increasing substitution of alkyl groups by halide reduces oxygen sensitivity. Alkaline hydrogen peroxide solution smoothly cleaves all three boron-carbon bonds.[79]

Oxygen will readily attack any aluminium-carbon bonds in a molecule[2b, 55,66] but the gallium trialkyls, while equally pyrophoric, react in a controlled oxygen supply to give R_2GaOR which is stable to further oxidation, as are the organogallium halides. These alkoxides are the origin of the sweet smells associated with the gallium trialkyls.[55] Et_3In behaves similarly[81] although at -78°C trimethylindium is believed to form $(Me_2In)_2O$.[60] The oxidation products of the thallium compounds have

not been studied in detail. Me_3Tl is pyrophoric in air[62] although pure Et_3Tl[63] and Ph_3Tl[65] are reported to be stable for short periods in dry oxygen.

8. Insertion Reactions

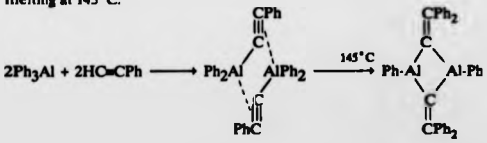
The insertion reactions that occur between alkenes and boron and aluminium alkyl and hydride species are of great importance from both an academic and an industrial viewpoint, and they are thus the subject of a very large body of literature. This includes a number of reviews[82-84] so these reactions will not be discussed here. It must suffice to say that the tendency of organometallic compounds of the lighter Group 13 elements to react cleanly with carbon-carbon multiple bonds complements the synthetic use of Group 1 and Group 2 organometallics which react more reliably with carbonyl groups.

A notable difference in behaviour between aluminium and gallium and indium is that while the former adds to the triple bond of terminal alkynes, gallium and indium alkyls eliminate alkane.[55,70,85]

$$Et_3Al + HC{\equiv}CH \xrightarrow{40\text{-}60^\circ C} Et_2AlCH{=}CHEt$$

$$Et_3Ga + HC{\equiv}CR \xrightarrow{50^\circ C} Et_2GaC{\equiv}CR + C_2H_6\uparrow$$

Triphenylaluminium however reacts according to the equation below to give a dimeric species which then undergoes an insertion reaction upon melting at 145°C.[86]



Gallium alkyls do undergo the growth reaction with ethene, but with less facility than aluminium alkyls.[55]

R_3M compounds (R = Me, Et; M = Al, Ga, In) do react with gaseous CO_2, but only one alkyl group reacts, to give the same dialkylmetal carboxylates as are produced in the reaction of R_3M and the appropriate acid.[87] Ph_3In reacts slowly with CO_2 to produce, after hydrolysis, a poor yield of benzoic acid.[88] Sulphur dioxide and sulphur trioxide can react with two or even all three C-Al bonds[89,90] and trimethylindium reacts with liquid SO_2 at -45°C to produce $(MeSO_2)_3In$.[91]

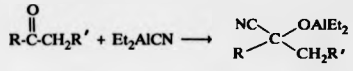
Reactions occur between trialkylaluminium reagents and many other carbonyl containing compounds, including aldehydes, ketones, acids, esters and amides, but the formation of dialkylaluminium hydrides can lead to reduction reactions competing with alkylation. Me_3Al, Et_3Al and Ph_3Al favour carbalumination. $(i\text{-}Bu)_3Al$ invariably effects hydralumination.[2b] Usually only one R-Al bond will insert into the C=O group. Vinyl-aluminium, alkyl-aluminium and aryl-aluminium bonds are more reactive with proton, halogen and carbonyl sources than are alkyl aluminium bonds[2b], so selective reactions can occur.[92]

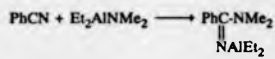
$$PhAlMe_2 + Ph_2C{=}O \longrightarrow Ph_3COAlMe_2$$

Nitriles are also attacked[93]

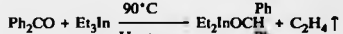
$$PhCN + Me_3Al \longrightarrow Ph(Me)C{=}N\text{-}AlMe_3$$

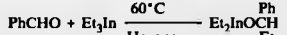
R_2AlZ (Z=CN, NR_2, SR) compounds can also undergo interesting reactions of this type.[94-96]



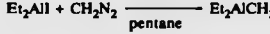


Triethylindium has been found to undergo insertion reactions with several compounds containing heteronuclear double bonds - benzophenone, benzaldehyde and phenylisocyanate.[97]





There are examples of Group 13 halides undergoing insertion reactions to yield organometallic products. Boron trichloride reacts in the vapour phase with acetylene to give 2-chlorovinyldichloroborane. At 100°C in the presence of catalysts it reacts further, forming *bis*(2-chlorovinyl)chloroborane and some *tris*(2-chlorovinyl)borane.[98] Diazomethane has also been shown to insert into MCl bonds of both trihalides and organometallic halides.[99]



The equivalent gallium compound has been prepared and used in the synthesis of $Et_2GaCH_2SiMe_3$ by reaction with $Me_3SiMgCl$.[100] The thallium compounds $(ClCH_2)_2TlCl$ and $Ar(ClCH_2)TlCl$ (Ar = Ph, 4-MeC_6H_4) are also known.[101,102] These compounds deserve more attention as they are potentially valuable synthetic intermediates.

III. The Organometallic Chemistry of Gallium and Indium

In addition to the general comparative reactions described above it is relevant to this thesis to deal in rather more detail with certain aspects of the compounds containing gallium and indium. As stated previously, this area has been the subject of a major, recent review by Tuck[2a] so this section is not comprehensive but instead highlights some informative examples, particularly from the literature subsequent to 1982.

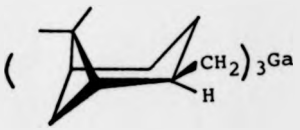
1. The Preparation of the Simple Trialkyls, Triaryls and Organometallic Halides

A. The Trialkyls and Triaryls

Several preparative methods are available, mostly the standard techniques used to prepare other metal alkyls.

1. Metal exchange with organomercury compounds. This is a particularly useful method for the preparation of Me_3Ga[103], $(vinyl)_3Ga$[104], Ph_3Ga[59], Me_3In[60] and Ph_3In[105], although it has the disadvantage that the reaction involves handling the highly toxic mercury dialkyls (or aryls) and requires high temperatures, typically 150°C for several days, so only thermally stable compounds can be prepared by this route. Use of highly activated indium metal, produced by the reaction of $InCl_3$ with potassium, greatly reduces the reaction times needed to prepare Me_3In and Ph_3In.[106]

2. The reaction of Grignard reagents with gallium and indium trihalides has been used to prepare a variety of R_3M compounds, including unusual species such as tri(*cis*-myrtanyl) gallium, below.[107]



If pure trialkyls are required, however, this method is only appropriate for compounds such as $(n\text{-Pr})_3Ga$,[108,109] and indium compounds[61,110] because these can be separated from the ether solvents used without the necessity of using temperatures high enough to decompose the products. An interesting variant of this process is the use of indium-magnesium alloys or mixtures with RBr in diethyl ether (R = Me, Et, n-Pr, i-Pr, n-Bu, i-Bu, s-Bu).[110] A similar method has been used to prepare trimethylgallium.[111]

3. Reaction of the trihalides with organolithium reagents. This method, using, for example, LiMe in Et_2O, also suffers from the disadvantageous presence of the co-ordinating solvent as above, but trimethylindium is commonly prepared in this manner.[112]

4. Redistribution reactions between gallium and indium halides and other metal alkyls. The most important example is the use of triethylaluminium to make Et_3Ga[113].

$GaCl_3 + 3Et_3Al \longrightarrow Et_3Ga + 3Et_2AlCl$

Three equivalents of KCl are added after the initial reaction to complex the aluminium as $K[Et_2AlCl_2]$. Traces of Et_3Al may be removed from the product by distillation with NaF, which complexes with Et_3Al but not Et_3Ga. $(i\text{-}Bu)_3Ga$ and Et_3In may also be obtained in this way, but to separate $(i\text{-}Bu)_3In$ from $(i\text{-}Bu)_3Al$ requires the addition of KF. Zinc alkyls have also been used in the preparation of trimethyl- and triethylgallium.[58,103] Like (1) these methods have the advantage of not requiring ether solvents which is important for semiconductor production if the ether cannot be removed completely.

In addition, several other methods have been used to obtain particular compounds:-

5. Reaction of R_3M (M = Ga, In) with acidic hydrocarbons such as phenylacetylene (12 h at 50°C) to give $[Me_2MC{\equiv}CPh]_2$[85] and Me_3In with CpH to give Me_2InCp.[114]

6. The electrolysis of $NaF.2AlEt_3$ using an indium anode yields Et_3In.[115]

7. Indium metal reacts with C_6F_5I in 6 hours at 160°C to produce $In(C_6F_5)_3$ in about 30% yield.[116,117] An alternative route to this compound is to react indium with $(C_6F_5)_2TlBr$. This reaction did not work with gallium.[118]

8. The displacement reaction of $(i\text{-}Bu)_3Ga$ with 1-decene to give $Ga(C_{10}H_{23})_3$.[113]

B. The Organometallic Halides

The organometallic halides are mostly prepared by similar methods to the trialkyls.

1. Use of Grignard reagents in an appropriate mole ratio. Examples include Ph_2InBr, $(Nap)_2InBr$[61] and $(C_6F_5)_nInCl_{3-n}$.[117]

2. Organolithium reagents can again be used, e.g. Bu_nGaCl_{3-n} (n = 1,2,3)[119] $RGaCl_2$ (R = Et, n-Bu, n-Bu, i-Bu, s-Bu, t-Bu)[120] and Me_2InX (X = Cl, I).[112] In this last example the reaction takes approximately two days, rather than the 30 minutes required to prepare Me_3In by the same method, because the initial product is a mixture of Me_3In and $InCl_3$, Me_2InCl being formed in a subsequent redistribution reaction.

3. The redistribution reaction between R_3M, isolated previously, and MX_3, is also a commonly used procedure. Examples include $Ga(CH_2SiMe_3)_nX_{3-n}$ (X = Cl, Br; n = 1,2)[121], Ph_nGaX_{3-n} (n = 1,2; X = Cl, Br, I)[122], Ph_nGaCl_{3-n}, including substituted phenyl derivatives[123], Ph_nInX_{3-n} (X = Cl, Br, I)[124], $In(CH_2SiMe_3)_nCl_{3-n}$[125] and $Me_2GaCl.OEt_2$.[46]

4. Reaction of R_3M with HX, e.g. Me_nGaCl_{3-n} (n = 1,2)[126], $In(CH_2SiMe_3)_nCl_{3-n}$.[125]

Other processes which have been used occasionally are as follows:

5. The reaction of Me_4Si, $(Me_2SiO)_4$, $(Me_3Si)_2O$ or Me_4Ge with gallium trichloride produces $MeGaCl_2$. Under similar conditions

Me_4Sn yields a 1:1 adduct, $Me_3SnClMeGaCl_2$ which on heating yields only the starting materials. Use of Me_3SiEt yields mainly $MeGaCl_2$, use of Me_3SiPh yields mainly $PhGaCl_2$, and Me_3SiCH_2Cl produces only $MeGaCl_2$.[127-129]

6. The reaction of R_3M and $BF_3{\cdot}OEt_2$ produces organometallic fluorides, R_nMF_{3-n}.[11,112,130]

7. The addition of $HGaX_2$ (X = Cl, Br) across a carbon-carbon double-bond yields $RGaX_2$ (R = Et, n-Pr, C_7H_{15}, cyclohexyl).[131,132]

8. Halogenated methanes react with Et_3In to give Et_2InX (X = Cl, Br, I).[133,134]

9. Halogens react with Ph_3Ga[122], Ph_3In[105] to give Ph_nMX_{3-n} compounds. Oxidation of CpIn by iodine yields $CpInI_2$.[42]

10. Indium metal has been reported to react slowly with many organic bromides and iodides to give mixtures analysing as $R_3In_2X_3$ (R = Me, Et, n-Pr).[135,136] Activated indium is more reactive,[137,138] and allows aryl compounds R_2InX (R = Ph, p-tolyl; X = Br, I) to be prepared.[139] Gallium can also be made to react,[140,141] and with half of an equivalent of iodine present, ultrasonic irradiation produces $RGaI_2$.[142]

$$Ga + \tfrac{1}{2}I_2 + RI \xrightarrow{\text{Ultrasound}} RGaI_2$$

11. Tuck[143] has prepared a number of neutral adducts of organoindium halides by an electrolytic method in cells of the type

$$Pt_{(-)} \mid RX + MeCN + bipy \mid In_{(+)}$$

2. Functionalised Organometallic Compounds

In addition to the wide range of simple trialkyls and triaryls listed by Tuck[2a] and the halides derived from them, a small number of organometallic compounds of gallium and indium have been reported that contain functionalised organic groups that are potentially of synthetic use. These are not just of academic interest, but could have practical applications - the possible hydrolytic stability of the dialkylmetal species could lead to organometallic drugs, for example. The known compounds include the halomethyl derivatives discussed earlier, $In(CH_2CH_2CN)_2I$ prepared electrochemically[144] and $In(CH_2CO_2Et)_2Br$, from $BrCH_2CO_2Et$ and activated In.[145] The preparation of a compound analysing as $Br_3In_2(CH_2CO_2Et)_3$ is described in Appendix B. Finally, $R_2InCH_2NO_2$ (R = Me, Et) and $Et_2InC(NO_2)Me_2$ have been prepared[146] by the reactions of the type:-

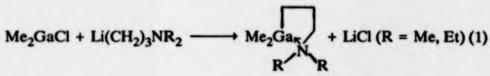
$$Me_3In + CH_3NO_2 \longrightarrow Me_2InCH_2NO_2 + CH_4\uparrow$$

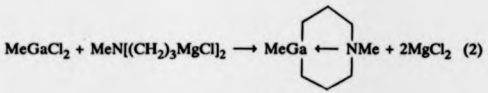
3. Neutral Adducts

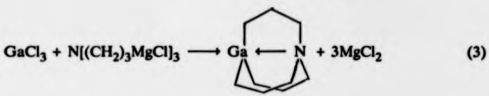
A list of the known adducts of R_3M species was included in the review by Tuck.[2a] Over thirty neutral ligands have been used, incorporating N, P, As, Sb, O, S, Se and Te donor atoms. The majority of these, however, are adducts of Me_3M with monodentate ligands and very few X-ray diffraction studies have been reported for this type of

compound - far fewer than of products of alkane elimination reactions, as will be seen in the next section.

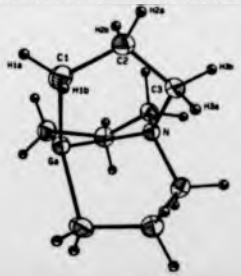
The most notable recent development in this area is probably the synthesis of a number of intramolecular complexes, particularly the series of gallium compounds prepared by Schumann and co-workers, shown below.[147]



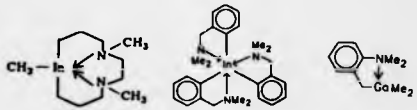




A crystal structure, shown below, has been obtained for (3).[147]

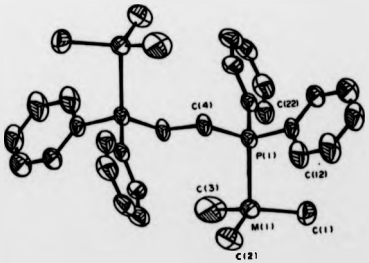


A subsequent paper reports a range of compounds similar to (1) above but with a greater range of alkyl chain lengths, including the indium equivalents.[148] The compound (4) has also been prepared.[149] Some intramolecularly stabilised aromatic compounds (5) and (6) have also been prepared.[150,151]



(4) (5) (6)

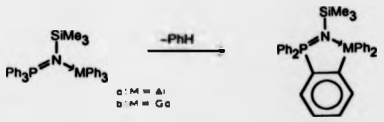
A range of complexes between R_3M and aryl phosphines have now been reported.[152,153] These include adducts formed with the polydentate phosphines "diphos", "triphos" and "tetraphos", but all have a 1:1 metal to phosphorus ratio. The structure of $(Me_3In)_2$. diphos is shown below.



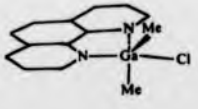
Tetramethyldiphosphine adducts have also been prepared.[154] Organo-phosphorus ylides will also form adducts.[155]

$$Me_3P = CH_2 + R_3M \longrightarrow Me_3\overset{+}{P}CH_2\overset{-}{M}R_3 \text{ (M = Ga, In, Tl; R = Me, Et)}$$

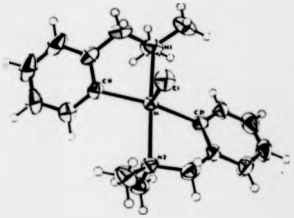
The 1:1 adduct of triphenylgallium with $Ph_3P = NSiMe_3$ loses a mole of benzene at 230°C via an ortho-metallation reaction of the phenyl ring to give the structure below.[156,157]



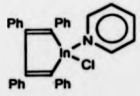
Even less work appears to have been done on the co-ordination chemistry of the organometallic halides. Again, most of the donors used have been nitrogen or oxygen based, including polydentate ligands. In most cases the acceptor species used has been Me_2MX (X = Cl, Br, I) and $MeMCl_2$, especially when M = In[70,112,158] although a greater variety of 2,2′-bipyridine adducts have been prepared electrochemically.[143] Again, few X-ray crystallographic studies have been conducted. Such studies could be rewarding - one of the few that has been carried out is on the 1,10-phenanthroline adduct of the Me_2GaCl, which has the interesting five co-ordinate structure shown.[159]

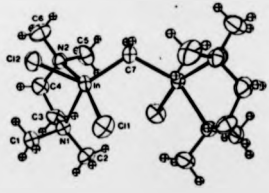


An intramolecularly bonded species, related to the tris complex noted earlier, is known.[150,160] The indium environment is essentially trigonal bipyramidal.



Other interesting compounds, prepared more recently, include the two shown below,[161,162] the second of which has also had its crystal structure determined.





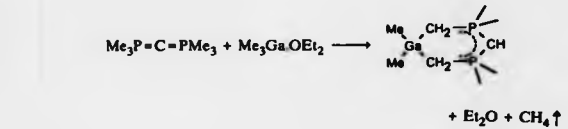
4. Reactions of R_3M with Acids

The main features of this reaction - the initial formation of an unstable complex and the stability of the dialkyl metal derivatives - have been noted already. Most of the compounds that will now be discussed are products of reactions using trimethylgallium and trimethylindium. Even the reactions of the triethyl- and triphenyl-metal derivatives have been much less well researched. The most convenient arrangement of

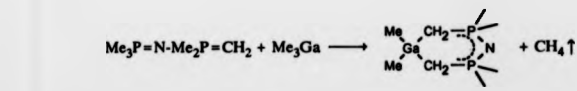
this section is in terms of ligand type. Particular emphasis will be placed on ligands based on nitrogen donors, and those, such as carboxylates, which are isostructural with the amidines used in Chapter 2.

A. Metal-Carbon Bonds

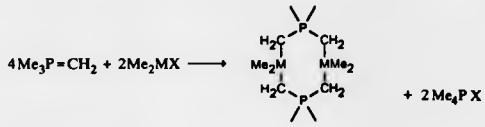
Relatively few C-H bonds are reactive enough to allow R_2MR' compounds to be synthesised by alkane elimination, but some reactions of this type have been performed successfully. Me_2InCp, $Me_2GaC{\equiv}CPh$ and $Me_2InCH_2NO_2$ were mentioned earlier, but more complex species have also been prepared by this method. The bisphosphorane, $Me_3P{=}C{=}PMe_3$ reacts with $Me_3Ga.OEt_2$ as shown below:-[163,164]



An equivalent nitrogen compound behaves similarly.[165]



A related compound can be prepared by a slightly different route, namely the reaction of the ylide $Me_3P{=}CH_2$ with Me_2MX.

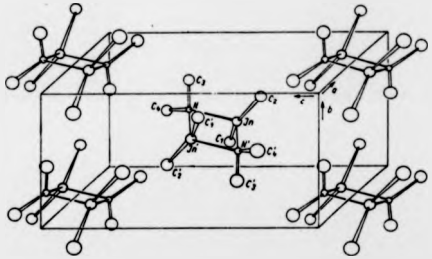


$4Me_3P{=}CH_2 + 2Me_2MX \longrightarrow$ + $2Me_4PX$

(M = Ga, In; X = Cl, Br)[166]

B. Metal-Nitrogen, -Phosphorus and -Arsenic Bonds

A typical example is $(Me_2InNMe_2)_2$ produced by reaction of Me_3In with Me_2NH. Its dimeric structure has been proven by an X-ray crystallographic study.[167] The unit cell is illustrated below.



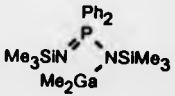
More recently, Storr and Thomas[168] have reported a series of related compounds prepared from Me_3M (M = Al, Ga, In) and the cyclic secondary amines aziridine, azetidine, pyrrolidine and piperidine. Molecular weight determinations were carried out and the trends discussed. Essentially, the aziridine derivatives were trimeric, while the other gallium and indium compounds were dimeric. The diethylgallium-aziridine compound was dimeric.

A slightly more complex nitrogen ligand is N,N′-dimethyl-acetamidine, which also reacts with R_3M (M = Al, Ga, In: R = Me, Et) to give a dimeric product with a puckered, eight-membered ring.[169,170]

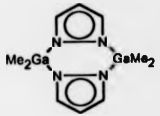
N,N′,N″,N‴-tetramethyloxamidine reacts with two equivalents of Me_3M (M = Ga, In) to form a virtually planar bicyclic system.[171] These compounds will be discussed in more detail in Chapter 2, in comparison with related compounds we have prepared.

The isolectronic triazene compounds have been prepared. Dimethylgallium-1,3-diphenyltriazene is believed to be monomeric, rather than the expected dimer.[172] Barron *et al*, apparently unaware of this work, found that all three metal methyl groups will react after 12 hours at 110°C, to form $(dpt)_3M$ (M = Al, Ga, In), but did not isolate any $dpt.MMe_2$ compounds.[173]

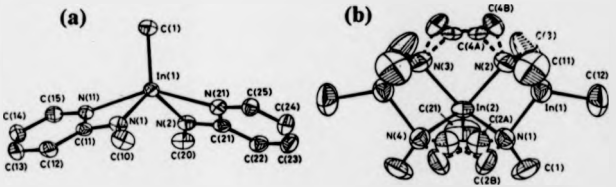
A similar phosphorus containing compound, $Me_3SiN=P(Ph_2)NHSiMe_3$, also eliminates methane on reaction with Me_3M (M = Al, Ga, In) to give a monomeric product.[174]



A series of pyrazole derivatives have been produced by reaction with trimethyl- and triethyl-gallium and $Me_3N.GaH_3$.[175] These are believed to exist in solution with a boat conformation of the dimeric N_4Ga_2 ring. The solid dialkylgallium compounds are air stable.

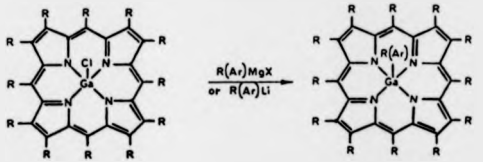


Two interesting compounds with five-co-ordinate square-pyramidal indium atoms have been prepared:[176] $MeIn[NC(CH)_4N]_2$ (a) and $MeIn\{[MeN(CH_2)_2NMe]Me_2In[MeN(CH_2)_2NMe]Me_2In\}$, (b)



A fairly recent area of study initiated by Robinson and co-workers is that of organogallium compounds with macrocyclic ligands. A range of these have now been prepared, most of which contain nitrogen donor atoms. These will be discussed in Chapter 3, when two new complexes will be reported. The corresponding indium compounds do not appear to have been prepared.

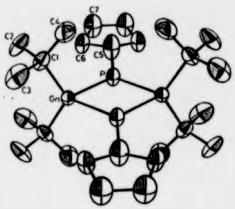
Another major class of cyclic nitrogen-containing ligand is the porphyrins. A number of examples of organogallium and organoindium-porphyrin complexes have been reported, mostly by Guilard and co-workers.[177-179] These were prepared by alkylation of the corresponding



metal chloro-species with Grignard reagents or organolithium reagents, but they could, in principle, be obtained via the direct reaction of the metal trialkyls with free porphyrins. Initially, this would probably yield the unreported dialkyl-metal complexes, but heating of these should cause the elimination of a further mole of alkane, as was observed for the macrocyclic complexes reported in Chapter 3. The crystal structure of methyl(tetraporphinato)indium(III) has been determined.[180] The indium atom is in a square based pyramidal environment, as would be expected.

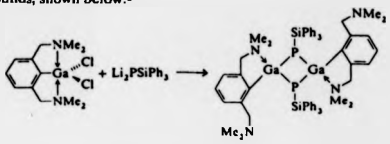
A large number of compounds containing the R_2PMR_2 and R_2AsMR_2 moieties are now known, stimulated primarily by the search for organometallic semiconductor precursors not covered by existing patents. It is therefore necessary to limit this discussion to just a few recent examples. Some of these were prepared by the displacement of halide from organometallic halides rather than by alkane elimination. These compounds tend to be dimeric, with four-membered rings essentially like that of $(Me_2InNMe_2)_2$, but trimeric structures are also common.

A good example of a dimeric structure is $[(t\text{-}Bu)_2GaP(H)(cyclopentyl)]_2$ which has a planar Ga_2P_2 core as shown below.[181]

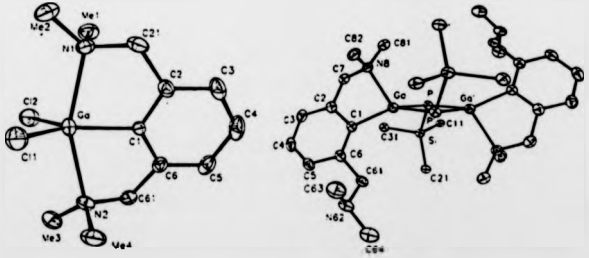


In contrast, when the cyclopentyl group is replaced by another hydrogen atom the structure is trimeric.[182]

Finally, the use of aromatic substituents with a donor side-chain again provides additional stabilisation, leading to the two interesting compounds, shown below:-[183]



The solid state structures of both have been determined:-



C. Group 13 Metal-Group 16 Bonds

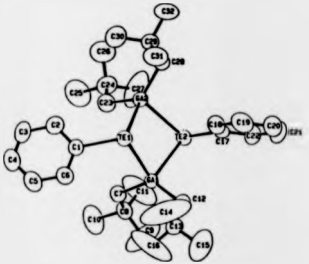
(i) Hydroxides, Alkoxides, Aryloxides and Related Species

The reactivity of R_3M towards water has been discussed already. Me_2GaOH has been isolated and characterised. It is a white crystalline solid, soluble in many organic solvents.[184] In solution in benzene it is polymeric, but the solid is a tetramer[185] with a puckered Ga_4O_4 ring. On heating to 150°C for 6 hours, methane is lost to give (Me_2GaO).[184] $[(Me_2Ga)_2O]_n$ has also been claimed as the hydrolysis product.[186] It is possible that the product of the hydrolysis reaction varies with experimental conditions. Me_2InOH does not appear to have been prepared.

Unsurprisingly, alcohols and phenols also react with trimethylgallium and analogous indium compounds are known. Methanol is typical, reacting to give Me_2GaOMe. This product and the equivalent sulphur and selenium compounds, are believed to be dimeric with the Group 16 atom in the bridge.[187] The dimeric structure of the sulphur and selenium compounds, but not the methoxide, is destroyed by the addition of trimethylamine and $Me_2GaER.NMe_3$ (E = S, Se) complexes are formed.

Me_2InOMe is a colourless glassy material which cannot be crystallised, suggesting that it is polymeric in the solid state,[21] but Me_2MOBu^t (M = Ga, In) are dimeric. Trivinylgallium also reacts with methanol, to give $(vinyl)_2GaOMe$, while dimethyl(vinyl)gallium reacts to give dimethylgallium methoxide and ethene.[188] The aryloxides Me_2GaOPh and $Me_2GaOC_6H_4Bu^t$ are easily prepared and are dimeric.[187] Again, the corresponding thio- and seleno- compounds are known.[187] Ph_3M (M = Ga, In) also react to give both Ph_2MSR and $PhM(SR)_2$ species. (R = $C_{12}H_{25}$).[189,190] A tellurium compound, $[(Me_3CCH_2)_2GaTePh]_2$ is

now known although it was prepared by displacement of chloride by LiTePh and not by alkane elimination.[191] The structure contains a Ga_2Te_2 core, as shown below.



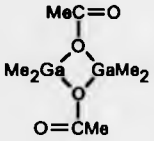
The reaction of Me_3M and R_3SiOH also gives dimeric derivatives $(Me_2MOSiR_3)_2$ (M = Ga, In; R = Me, Ph).[192] The germanium species can be made by similar methods.[193]

(ii) Organometallic Carboxylates and Thiocarboxylates

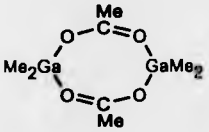
A range of carboxylates and thiocarboxylates is known. They are of particular interest because they are an important example of a ligand isoelectronic with the amidines used in Chapter 2, and therefore might be expected to adopt similar structures.

Trimethylgallium reacts with one equivalent of acetic acid in benzene, eliminating methane and forming Me_2GaO_2CMe, shown by molecular weight determinations to be dimeric in acetone solution.[187] The infra-red spectrum is consistent with

three atom bridges in structure (B), not (A).[172] The solid state structure is not known.

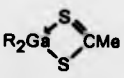


(A)

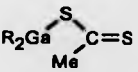


(B)

$MeGa(O_2CMe)_2$, prepared from $Me_3Ga.OEt_2$ and excess acid, is also associated in benzene solution. The solid is a polymer with bridging acetate groups and two inequivalent sets of gallium atoms. One is in a distorted trigonal-bipyramidal GaO_4C environment, the other with distorted tetrahedral GaO_3C stereochemistry.[194] R_2GaS_2CMe (R = Me, Et) is known to be monomeric, from vibrational spectra[195] and is bidentate, (A), not (B)



(A)



(B)

The equivalent indium compounds have been investigated more systematically. Solid Me_2InO_2CMe is also polymeric, with

six co-ordinate indium atoms.[196] It is depolymerised by bases such as pyridine to form adducts.[197] Diethylindium acetate has a similar structure.[198,199] In the related mono-thiocarboxylate, $Et_2InO(S)CMe$, only the oxygen atom is involved in bridging, and the indium is five co-ordinate.[200] Again, the dithiocarboxylates, $R_2In(S_2CMe)$, (R = Me, Et) are monomeric.[195]

The aryl compounds Ph_2MO_2CR and $PhM(O_2CR)_2$ can also be prepared. (M = Ga, In; R = Me, Et).[201,202]

Bis(dimethylgallium)oxalate has been prepared,[203] and has a very similar structure to the oxamidine complex noted earlier.

(iii) Other Metal-Oxygen Bonded Compounds

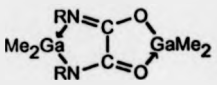
Dimethyl-gallium and -indium acetylacetonates are well known and readily prepared.[21, 187] A significant number of derivatives of other protic acids are known, including several -sulphur and -phosphorus oxy-acids.[91,172,188] These cannot be discussed in detail here, and the reader is referred to Tuck[2a] for further information.

D. Compounds Containing Metal-Nitrogen and Metal-Oxygen Bonds

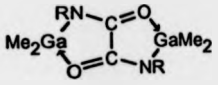
The most important members of this category, again because of their relevance to the amidines discussed later, are the amides. Both the dimethyl- and diethyl-gallium and indium derivatives of N-methyl acetamide are known, and their spectra have been interpreted in terms of a bridged dimer structure with an eight-membered ring.[204]

Oxamide derivatives have also been reported.[205] These have the same basic structure as the oxamidine and oxalate complexes, already noted, but in addition, *cis* and *trans* isomers exist.[205,206] In the *cis*

complex, (A) below, one gallium atom is co-ordinated by two nitrogen atoms, the other by two oxygen atoms. In the *trans* complex (B) the two gallium atoms are in an identical environment, each co-ordinated by one nitrogen and one oxygen atom.



(A)



(B)

A number of other types of organic compounds containing acidic hydrogens are capable of acting as bidentate or polydentate ligands with both M-O and M-N bonds. A variety of interesting structures are known including species derived from oximes, 8-hydroxyquinoline, ethanolamine and N,N-diacetylhydrazine, but again space does not permit their discussion here.

E. Miscellaneous Compounds

The gallium and indium trialkyls have been used to produce compounds containing gallium and indium bonded to a number of other elements that have not been discussed above. Metal-boron bonds have been formed in reactions between R_3M and complex boron hydrides. The trialkyls also react with some organometallic transition metal compounds to form new metal-metal bonds. Again, Tuck discusses these in more detail.[2a]

CHAPTER 2

A Study of Organogallium-Amidine Complexes

CHAPTER 2 A Study of Organogallium-Amidine Complexes.

Introduction

The organogallium-amidine complexes are of both intrinsic and applied interest. Amidines are an example of the pseudo-allyl class of ligands, so, as was noted in Chapter 1, they are either iso-electronic with, or closely related to, a number of better known organic species, including those shown in Table 1.

Table 1. Some Examples of Pseudo-Allyl Ligands.

Group	Name
	allyl
	amidine
	triazene
	amide
	carboxylic acid

These groups are all potentially bidentate ligands, and a number of co-ordination modes are possible. Structural information is therefore particularly valuable. As more becomes available, instructive comparisons between organogallium complexes with these related ligands should be possible.

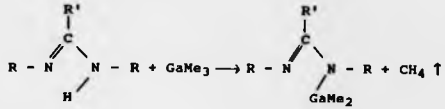
The amidine complexes also have potential for application as a gallium source in the production of electronic materials such as "III-V" semiconductors because they do not contain oxygen and they are often appreciably volatile. Thermal decomposition reactions of such compounds are therefore of some interest and importance.

Only two organogallium-amidine complexes have been reported previously.[169-171] The primary aim of this present work has been therefore to extend the range of known compounds, and to study their properties. This chapter reports the preparation and some properties of fourteen new dimethylgallium-amidine complexes. Also included is the result of an X-ray crystallographic study of the molecular structure of the compound dimethylgallium-N,N′-diphenylbenzamidine. As outlined below this shows a significant and interesting difference from the other known structures of alkyl gallium-amidine derivatives.

The amidines used here have the structure $RNC(R')N(H)R$ (R,R′ = H, alkyl, aryl). The trivial names for amidines, used herein, are based on the amide or acid produced by hydrolysis. Thus, when $R' = H$ the compound is known as a formamidine; $R' = CH_3$, an acetamidine and $R' = C_6H_5$, a benzamidine. The systematic names used in Chemical Abstracts, treat amidines as amides of the corresponding imidic acid. Formamidine is therefore methanimidamide, acetamidine is ethanimidamide and benzamidine is benzenecarboximidamide.

Preparation of Dimethylgallium-Amidine Complexes

The dimethylgallium-amidines were prepared by mixing equimolar quantities of trimethylgallium and the amidine in toluene or hexane solution. The reactions proceed easily, the evolution of the one mole of methane commences at low temperatures (approximately -60°C) and is usually complete by the time the solution has warmed to room temperature. Removal of the solvent under vacuum leaves the products as white or pale yellow solids.



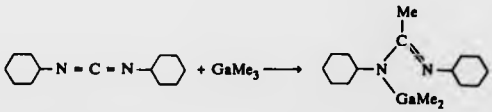
The new compounds prepared in the course of this work are listed below:-

Table 2. New dimethylgallium-amidine complexes prepared during this study.

R	R′	R	R′
Ph	Ph	p-FPh	Me
p-MePh	Ph	p-ClPh	Me
p-(i-Pr)Ph	Ph*	cyclohexyl	Me
H	Ph	H	Me
Ph	Me	Ph	H
p-MePh	Me	o-MePh	H*
o-MePh	Me*	cyclohexyl	morpholine

* Included on the basis of mass spectra data only.

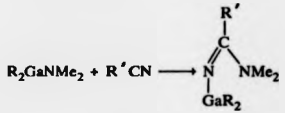
Two alternative routes to this class of compounds were tried, but with very limited success. No solid product could be isolated after the attempted insertion reaction between trimethylgallium and dicyclohexylcarbodiimide below:-



This is consistent with the work of Weidlein *et al.*, who found that trimethylaluminium reacts with *bis*(trimethylsilyl)carbodiimide to give a solid

monomeric insertion product, equivalent to that shown above, but $GaMe_3$ and $InMe_3$ only form liquid 1:1 adducts.[207] Attempts were also made to react the gallium(III) chloride adduct of N,N′-diphenylacetamidine with three equivalents of methyllithium. ^1H N.M.R. spectra of the product are essentially correct for the dimethyl gallium complex, but also showed the presence of considerable amounts of diethylether which proved impossible to remove. Elemental analyses were therefore not obtained for this product.

A possible route to related asymmetric compounds that was not attempted, due to shortage of time, is a reaction of the type:-



Equivalent aluminium reactions (R = Et, R′ = Me, benzyl, aryl) are known to occur.[96] It is also conceivable that organogallium-phosphine complexes, $R_2GaPR'_2$, might also react in a similar manner, but no work in this area has yet been conducted.

Some Aspects of the Chemical Reactivity of the Complexes.

Air Sensitivity

All the dimethylgallium-amidine complexes prepared here are air sensitive to some extent. Quantitative measurements have not been made, but the evidence, which will be discussed in more detail later, suggests that they hydrolyse back to amidine and a dimethylgallium species, probably Me_2GaOH or $(Me_2Ga)_2O$. However, the compounds can be conveniently handled under dry nitrogen and manipulations were therefore carried out in a nitrogen-filled glove box or Schlenck line.

Reactions with excess Amidine

Three dimethylgallium-amidine compounds have been heated with excess amidine to investigate whether further gallium-methyl groups will react. Both the yields of methane and the ^1H N.M.R. spectra suggest that reaction does occur, but it again proved impossible to isolate pure products, primarily due to their low solubility. In view of the difficulty in attempts to purify the compound it is also possible that N.M.R. spectra may not be representative of the bulk material.

In another experiment dimethylgallium-N,N′-diphenylacetamidine was heated with a large excess (about 3½ equivalent) of amidine. Methane was first evolved around 90°C while the mixture was still solid. More was produced after the mixture melted at about 125°C giving a total yield of approximately two equivalents. The reaction mixture was maintained at 145°C for about 10 hours, by which time it had solidified. Excess amidine was then sublimed out, and the ^1H N.M.R. spectrum of the residue showed that no Ga-CH_3 protons remained, but two CH_3 resonances were present and elemental analyses also showed that the product was impure.

In an attempt to make a mixed amidine compound dimethylgallium-N,N′-diphenylbenzamidine was heated with one mole equivalent of N,N′-diphenylacetamidine. Again, the reaction started abruptly at about 90°C with partial melting. Approximately one equivalent of methane was evolved, but the ^1H N.M.R. spectrum showed the material produced to contain fewer than the three Ga-CH_3 protons per molecule expected for methylgallium-(N,N′-diphenyl benzamidine)(N,N′-diphenylacetamidine).

Reactions between dimethylgallium-N,N′-di(p-chlorophenyl)acetamidine and one and two moles of additional amidine were also performed under similar conditions. Methane was again evolved, but neither the *bis*- nor *tris*-amidine-gallium compounds could be obtained pure. The preparation of *tris*[di(p-chlorophenyl)acetamidine] gallium was also attempted by melting three

equivalents of the amidine with gallium(III)chloride at 140°C. The presence of a large quantity of excess amidine, elemental analysis and mass spectral evidence shows that only one mole of HCl is lost, forming the dichlorogallium-amidine complex.

Thermal Decomposition Reactions

In an effort to gain some insight into the thermal decomposition of these compounds a number of thermogravimetric analysis (T.G.A.) and differential thermal analysis (D.T.A.) experiments were carried out by our collaborating body, Octel. The results are summarised in Table 3, and discussed briefly here. They are not especially informative, but a number of conclusions may be drawn. Points worthy of note are as follows. All the compounds decompose before subliming at atmospheric pressure, and the T.G.A. plots are fairly smooth, sigmoid curves for all except one compound. The plot for the dimethylgallium derivative of N,N′-di(p-fluorophenyl)-acetamidine shows a double sigmoid curve indicating that the decomposition in this case is, to some extent, a stepwise process. However, the transitions are still rather poorly defined, there being no definite plateaux in the T.G.A. plot except for the initial and final weights. No steps can thus be certainly assigned to likely stages of thermal decomposition. The dimethylgallium complexes decompose mostly between 200-300°C, except the substituted benzamidine derivatives which decompose 50-100°C higher. The typical residual fragment size is about 100 mass units, but there is considerable variation. The value of 60 for one run of dimethylgallium-N,N′-di(p-chlorophenyl)acetamidine is probably false since the other gives a more "normal" value of 100. Several results are within the range 84-90. Relatively high values also occur, and the di(p-fluorophenyl)acetamidine derivative is again anomalous, with consistent values of 142 and 145. Even if the assumption is made that these fragments in each case represent a single compound, its identity is uncertain. A value of 84 could be explained by $(MeGa)_n$ which has been claimed to be the

Table 3. Summary of T.G.A. Results

Compound	M.W.	Final wt. %	Final fragment	Approx. Decomp. temp(°C)	T.G.A. curve shape	Max temp (°C)	Date of Run
Dimethylgallium-N,N′-diphenylbenzamidine	371.13	26.76	99.31	c 250	Smooth Sigmoid	498.81	31.5.89
Dimethylgallium-N,N′-di(p-tolyl)benzamidine	399.18	33	132	c 350	Smooth Sigmoid	500	4.7.89
Dimethylgallium-N,N′-di(p-isopropylphenyl) benzamidine	455.29	27 (at 600°C)	123	c 300	Smooth Sigmoid	1000	5.1.90
Dimethylgallium-N,N′-diphenylacetamidine	309.06	29	90	c 250	Smooth Sigmoid	500	9.5.89
Dimethylgallium-N,N′-di(p-tolyl)acetamidine	337.11	30	101	c 250	Smooth Sigmoid	500	4.7.89
Dimethylgallium-N,N′-di(p-tolyl)acetamidine	337.11	25	84	c 400	Smooth Sigmoid	1000	20.7.89
Dimethylgallium-N,N′-di(p-fluorophenyl) acetamidine	345.04	41	142	c 250 & c 425	Double Sigmoid	500	3.7.89
Dimethylgallium-N,N′-di(p-fluorophenyl) acetamidine	345.04	42	145	c 275 & c 425	Double Sigmoid	1000	20.7.89

Compound	M.W.	Final wt. %	Final fragment	Approx. Decomp. temp(°C)	T.G.A. curve shape	Max temp (°C)	Date of Run
Dimethylgallium-N,N′-di(p-chlorophenyl) acetamidine	377.95	16	60	c 250	Smooth Sigmoid	418	4.7.89
Dimethylgallium-N,N′-acetamidine	377.95	26.5 (at 600°C)	100	c 275	Smooth Sigmoid	1000	5.1.90
Dimethylgallium-N,N′-dicyclohexylacetamidine	321.15	26 (at 500°C)	84	c 220	Smooth Sigmoid	1000	8.1.90
Dimethylgallium-N,N′-dicyclohexylacetamidine	321.15	26	84	c 200	Smooth Sigmoid	500	25.6.90
Dichlorogallium-N,N′-di(p-chlorophenyl)acetamidine	418.79	13.1 (at 500°C)	54	c 325	Smooth Sigmoid	540	27.6.90
Dichlorogallium-N,N′-di(p-chlorophenyl)acetamidine	418.79	17	71	c 350	Smooth Sigmoid	600	28.6.90
Galljum(III)chloride-N,N′-di(p-chlorophenyl) acetamidine	455.25	14 (at 500°C)	64	c 350	Smooth Sigmoid	600	28.6.90
Galljum(III)chloride N,N′-di(p-chlorophenyl) acetamidine	455.25	12	54	c 325	Smooth Sigmoid	500	29.6.90
Galljum(III)chloride-N,N′-di(p-chlorophenyl) acetamidine	386.36	19	73	c 350	Smooth Sigmoid	600	28.6.90

product of the thermal decomposition of $GaMe_3$.[208] Gallium nitride is probably a more likely product, but it sublimes at 800°C.[1] Values around 100 are consistent with either $(Me_2Ga)_n$ or $(MeGaN)_n$ with the latter being a more likely possibility. Obviously conclusions about the nature of the residual solid are tentative, but this area was not within the mainstream of the research being undertaken, and more complete studies were therefore not carried out.

The gallium(III)chloride-amidine adducts $RNC(R')N(H)R.GaCl_3$ (R = Ph, p-ClPh; R' = Me) decompose between 300°C and 400°C. Again, the T.G.A. curves are smooth and featureless. The plots for $GaCl_3$ adducts show possible evidence of hydrogen chloride loss at about 250°C, (the reaction performed earlier suggest this can occur below 150°C). The residual masses are lower than for the dimethylgallium complexes, in the range 54-73. Such small values are particularly difficult to explain in terms of a chemically discrete residue. The most probable residues - gallium metal, gallium nitride or gallium(I) chloride- do not account for these values satisfactorily, so here also, further studies are necessary before definite conclusions can be drawn.

Spectroscopic Properties of the Dimethylgallium-Amidine Complexes.

Nuclear Magnetic Resonance Spectra.

^1H N.M.R. spectra have been recorded routinely during the course of this work and have proved useful in verifying the stoichiometry of the reaction products. Details of the spectra of individual compounds are reported in the experimental section. Only the general features of the spectra will be discussed here. Some typical spectra of dimethylgallium complexes are reproduced in Figures 1 and 2. The most important feature is the presence of the resonances due to the gallium-methyl protons which have chemical shifts close to, or even coincidental with, that of tetramethylsilane (T.M.S.). Therefore, dichloromethane was the internal reference used normally since the chemical shift, 5.34 p.p.m. in $CDCl_3$, is well away from aromatic, aliphatic and

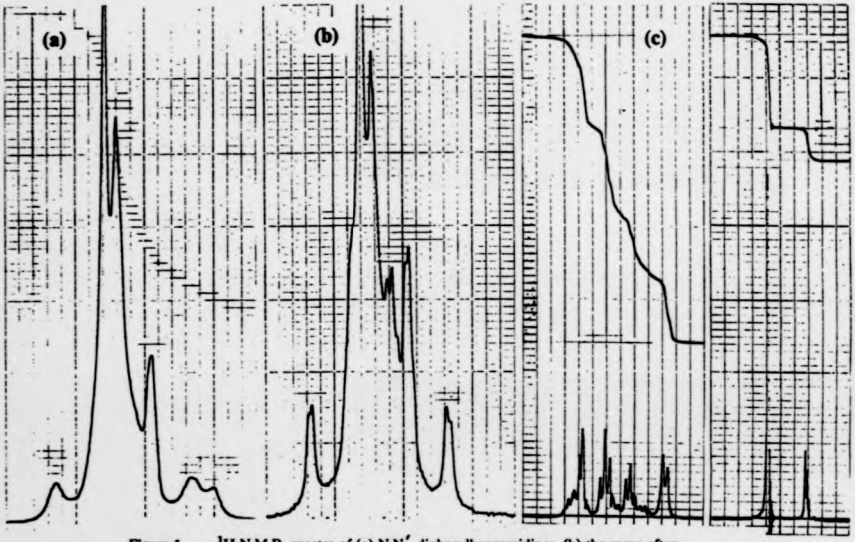


Figure 1. ^{1}H N.M.R. spectra of (a) N,N′-diphenylbenzamidine; (b) the same after shaking with D_2O; (c) dimethylgallium derivative.

Note - chemical shifts omitted, but relative positions of spectra approximately correct.

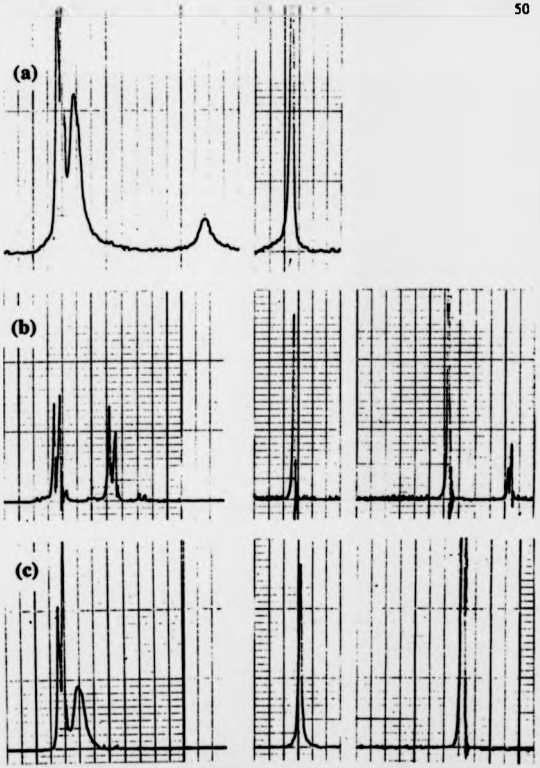


Figure 2. ^1H N.M.R. spectra; (a) N,N'-di(p-chlorophenyl)acetamidine; (b) dimethylgallium-N,N'-di(p-chlorophenyl)acetamidine; (c) the same, after exposure to air.

Note - chemical shifts omitted, but relative positions of spectra approximately correct.

organometallic proton resonances. An unexpected feature of the spectra is that the gallium-methyl region usually contains one or more smaller resonances. The origin of this effect, which varies between samples, is not certain. Because the total gallium-methyl integrals are correct, it cannot be due to co-ordinated trimethylgallium. The typical lack of equivalent peaks in the C-CH_3 region of the spectra of the acetamidine derivatives suggests that it is probably not explained by a slow monomer-dimer exchange process. It would also be expected that if these peaks were primarily due to impurities, such amounts (variable, but up to the 25% shown in Figure 1) would lead to unacceptably poor analytical results. The spectra of the dimethylgallium derivatives also have a more structured aromatic region than the parent amidines, as seen in Figures 1 and 2.

Some ^{13}C N.M.R. spectra have also been recorded and these results are summarised in Table 4. The partial assignments of the aromatic carbon atoms are tentative, being primarily based on peak height. The spectra are consistent with the ^1H N.M.R. data in showing that the two N-aryl rings are equivalent on the N.M.R. time scale. In all cases the $GaCH_3$ resonances occur at about -6 p.p.m., which is much where they would be expected. The peaks consistently present around 144 p.p.m. are thought to be due to the aryl carbon atoms that are bonded to the amidine nitrogens. The carbon atom in the centre of the amidine unit, when located, seems to occur close to 170 p.p.m. The spectra of dimethylgallium-N,N′-diphenylbenzamidine, run in $CDCl_3$, C_6D_6 and $C_6D_5CD_3$ show that slight changes in chemical shifts occur when different solvents are used.

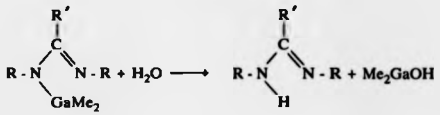
Samples of the pure dimethylgallium derivatives are usually stable in $CDCl_3$ for at least 24 hours if kept tightly sealed or under an inert atmosphere. The ^1H N.M.R. spectra of solid samples of dimethylgallium-N,N′-di(p-chlorophenyl)acetamidine that have been exposed to air or damp nitrogen (Figure 2) show a collapsed aromatic region, very similar to that of the amidine.

Table 4 ^{13}C NMR results (p.p.m.) for some dimethylgallium-amidine complexes

Compound (solvent)	$Ga^{13}CH_3$	$N_2C^{13}CH_3$	$Ar^{13}CH_3$	Ar	$N_2{}^{13}CC$
[PhNC(Me)NPh]$GaMe_2$($CDCl_3$)	-6.20	15.17	-	123.00 (?2 x CH), 123.19 (?4xCH), 128.93 (?4xCH). 144.49 (?2xCN)	*
[(p-MePh)NC(Me)N(p-MePh)] $GaMe_2$(CD_2Cl_2)	-6.40	15.24	20.73	123.27(4xCH), 129.77 (4xCH), 142.36 (?2xCN) Para quaternary carbon atom not positively identified.	? 174
[PhNC(Ph)NPh]$GaMe_2$($CDCl_3$)	-6.06	-	-	122.91 (?2xCH), 123.63 (?4xCH), 124.93 (?6xCH), 129.65 (?2XCH) 130.31 (?1xCH), 144.4 (?2xCN)	*
[PhNC(Ph)NPh]$GaMe_2$(C_6D_6)	-6.34	-	-	123.10 (?2xCH). 123.62 (?4xCH), 128.77 (?2xCH), 129.07 (?4xCH), 129.58 (?2xCH), 130.00 (?1xCH), 131.01 (?1x$^{13}CCN_2$)	*
[PhNC(Ph)NPh]$GaMe_2$($C_6D_5CD_3$)	-6.08	-	-	122.94 (?2xCH), 123.46 (?4xCH), 128.77 (?2xCH), 129.01 (?4xCH), 129.01 (?4xCH), 129.41 (?2xCH), 129.94 (?1x$^{13}CCN_2$), 130.09 (?1xCH), 144.10 (?2xCN)	167.31

* Not located

Only one singlet is found in the gallium-methyl region and it has a slightly different chemical shift to any of the peaks in the spectrum of the unreacted complex. The expected decomposition reaction is:-



No NH or OH resonances have been identified, possibly because they are very broad. It is also possible that very slow hydrolysis could lead to the formation of $(Me_2Ga)_2O$ rather than Me_2GaOH.

Infra-Red Spectra

Infra-red spectroscopy has been relatively little used due to the difficulty of detailed interpretation. Spectra of both Nujol and hexachlorobutadiene (H.C.B.D.) mulls of four amidines and their dimethylgallium derivatives have been recorded. The spectra of the amidines and complexes are generally rather similar. The significant differences between the complexes and parent ligands (i.e. peaks that are present in only one member of a pair of spectra, or show a considerable change in intensity) are summarised in Table 5. A more complete listing of the observed peaks is given in the Experimental Section.

Table 5. The differences between the I.R. spectra of the amidines and the dimethylgallium complexes.

Parent Amidine	Free Amidine	Dimethylgallium Complex
N,N′-diphenylbenzamidine	1492 m 1488 m 525 w	1612 m 1490 s 1425 w - m 592 w, br 570 w, br 530 w
N,N′-diphenylacetamidine	1542 s 520 s	1660 w 1542 m 1520 s, br 1420 s 590 m, br 580 m, br 530 w, br 520 w, br
N,N′-di(p-chlorophenyl) acetamidine		1515 s 870 w 580 w-m, br 525 w-m, br
N,N′-diphenylformamidine	1680 s 1230 w 900 m 765 s 755 s 600 w - m 520 w - m	1680 s 1562 s 1375 s 1230 m 760 s 575 m 520 m

s = strong
m = medium
w = weak
br = broad

All eight spectra contain strong bands at about 1588 and 1490 cm^{-1}. Peaks near 1630 and 1540 cm^{-1} are prominent in all spectra except those of N,N′-diphenylformamidine and its dimethylgallium complex. The bands around 1640 and 1588 cm^{-1} have been assigned to asymmetric CN_2 stretching and C=N stretching modes, respectively, in the free ligand ("Amidine I" bands). Those

around 1540 cm^{-1} are described as "Amidine II" bands, of complicated origin.[209] It is perhaps surprising that in the species reported here, relatively little change occurs in this region, upon reaction, and no consistent pattern emerges. With N,N′-dimethylacetamidine it was reported that the ν_{asym} (CN_2) band shifts from 1640 cm^{-1} in the amidine to 1552 cm^{-1} in the dimethylgallium derivative.[169] In *bis*(dimethylgallium)-N,N′N″,N‴-tetramethyl-oxamidine this peak occurs at 1604 cm^{-1}.[171] It must be remembered that in the compounds reported here, aromatic C-C stretches will also occur in this region.

The most important difference between the spectra of the free amidines and the complexes is the broad and poorly defined peaks which occur close to 580 and 530 cm^{-1} in the latter, hiding weaker but sharper bands in the ligand spectrum. These are in the expected position for the $GaMe_2$ asymmetric and symmetric stretches respectively.[2a] They are also consistent with the values reported for dimethylgallium-N,N′-dimethylacetamidine (557 and 518 cm^{-1})[169] and the dimethylgallium-oxamidine compound (566 and 530 cm^{-1}).

The bands, always broad, around 3200 cm^{-1}, which should include the N-H stretching frequencies are less prominent in the H.C.B.D. mulls of the dimethylgallium complexes.

Other bands cannot be assigned with confidence. Care must also be taken because the dimethylgallium complexes, especially that of N,N′-diphenylbenzamidine, is likely to be significantly soluble in Nujol so spectra may not always be directly comparable. Some amidine bands are known to be shifted significantly in solution.[209] Some reaction also occurs between both the amidine and complexes with H.C.B.D., the mulls slowly turning brown.

Upon hydrolysis the dimethylgallium bands remain, but a sharp peak appears at 3640 cm^{-1}. This may be due to dimethylgallium hydroxide co-ordinated by amidine. The OH stretch in pure, solid Me_2GaOH occurs at 3601 cm^{-1}, although this is shifted to 3643 cm^{-1} in CCl_4 solution.[72] Otherwise the spectra revert to that of the amidine.

The spectrum of a Nujol mull of the N,N′-di(p-chlorophenyl)acetamidine adduct of gallium(III) chloride has been obtained. A list of peaks is again included in the Experimental Section. The most important features are the intense NH peak at 3290 cm^{-1}, and what are presumed to be Ga-Cl stretches, at 495, 400, 375 and 350 cm^{-1}.

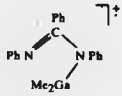
Ultra-Violet/Visible Spectra

UV/visible spectra were run for several amidines and the corresponding dimethylgallium derivatives, but were generally uninformative. Even when the amidine absorption was not hidden by aromatic peaks, it was only shifted by about 1 nm in the complexes. While not unexpected this was disappointing because spectra are easily obtained for very small samples.

Mass Spectra

Mass spectra have been obtained for all the dimethylgallium-amidine complexes except that with acetamidine. They provide valuable evidence that the intended products have in fact been formed. The electron impact (E.I.) and chemical ionisation (C.I.) spectra of all the compounds show molecular ions. Some spectra also show higher mass species, probably due to reactions in the source, but no dimer units are seen. Figures 3 - 6 show the significant ions of the E.I. spectra of four compounds, the dimethylgallium complexes of N,N′-diphenylbenzamidine, N,N′-diphenylacetamidine, N,N′-di(p-chlorophenyl)-acetamidine and N,N′-diphenylformamidine. The isotope ratios aid identification of gallium-containing fragments. In all cases the percentage relative intensities are given for the ^{69}Ga and, where applicable, the ^{35}Cl peaks. The C.I. spectra are similar, but show less fragmentation, as would be expected. The base peaks in the spectra of the N,N′-diphenyl substituted amidines shown are the same as those for the parent amidines, i.e. $[PhN{=}CR']^+$ for the benzamidine and acetamidine, and $[PhNH_2]^+$ for the formamidine.[210] The

Figure 3. **Fragmentation Scheme for Mass Spectrum of Dimethylgallium-N,N'-diphenylbenzamidine.**



370 (18.8%)

$\xrightarrow{-GaMe_2}$ $[C_{19}H_{15}N_2]^+$ 271 (12.5%)

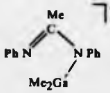
$\xrightarrow{-Me^-}$ $[C_{20}H_{18}N_2Ga]^+$ 355 (77.5%) $\xrightarrow{-CH_4}$ $[C_{19}H_{14}N_2Ga]^+$ 339 (3.7%) $\xrightarrow{-Ga^-}$ $[C_{19}H_{14}N_2]^+$ 270 (2.1%)

$\xrightarrow{-Ligand}$ $[GaMe_2]^+$ 99 (4.2%) $\xrightarrow{-C_2H_6}$ Ga^+ 69 (6.5%)

$\longrightarrow$ $[PhN{=}CPh]^+$ 180 (100%) $\xrightarrow{-PhCN}$ $[C_6H_5]^+$ 77 (40.2%) $\xrightarrow{-C_2H_2}$ $[C_4H_3]^+$ 51 (8.5%)

$\longrightarrow$ $[PhNHGa]^+$?
161 (18.4%)

Figure 4. **Fragmentation Scheme for Mass Spectrum of Dimethylgallium-N,N′-diphenylacetamidine.**



308 (6.1%)

$\xrightarrow{\cdot GaMe_2}$ $[C_{14}H_{13}N_2]^+$ 209 (23.6%)

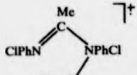
$\xrightarrow{\cdot Me}$ $[C_{15}H_{16}N_2Ga]^+$ 293 (49.2%) $\xrightarrow{\cdot CH_4}$ $[C_{14}H_{12}N_2Ga]^+$ 277 (4.3%) $\xrightarrow{\cdot Ga}$ $[C_{14}H_{12}N_2]^+$ 208 (2.7%)

$\xrightarrow{\cdot Ligand}$ $[GaMe_2]^+$ 99 (5.2%) $\xrightarrow{-C_2H_6}$ Ga^+ 69 (11.2%)

$\longrightarrow$ $[PhN=CMe]^+$ 118 (100%) $\xrightarrow{\cdot MeCN}$ $[C_6H_5]^+$ 77 (79.2%) $\xrightarrow{-C_2H_2}$ $[C_4H_3]^+$ 51 (26.5%)

$\longrightarrow$ $[PhNH_2]^+$ 93 (10.2%)

Figure 5. **Fragmentation Scheme for Mass Spectrum of Dimethylgallium-N,N'-di(p-chlorophenyl)acetamidine**



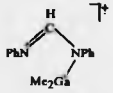
$\xrightarrow{-GaMe_2^{\cdot}}$ $[C_{14}H_{11}N_2Cl_2]^+$ 277 (7.3%)

$\xrightarrow{-Me^{\cdot}}$ $[C_{15}H_{14}N_2Cl_2Ga]^+$ 361 (95.0%) $\xrightarrow{-CH_4}$ $[C_{14}H_{10}N_2Cl_2Ga]^+$ 345 (8.8%)

$\xrightarrow{-Ligand}$ $[GaMe_2]^+$ $\xrightarrow{-C_2H_6}$ Ga^+ 99 (17.5%) 69 (30.0%)

$\longrightarrow$ $[ClPhN{=}CMe]^+$ $\xrightarrow{-MeCN}$ $[ClC_6H_4]^+$ $\xrightarrow{-C_2H_2}$ $[ClC_4H_2]^+$ 152 (66.6%) 111 (34.3%) 85 (1.6%)

Figure 6. **Fragmentation Scheme for Mass Spectrum of Dimethylgallium-N,N'-diphenylformamidine**



294 (12.6%)

$\xrightarrow{-GaMe_2^{\cdot}}$ $[C_{13}H_{11}N_2]^+$ 195 (18.8%)

$\xrightarrow{-Me^{\cdot}}$ $[C_{14}H_{14}N_2Ga]^+$ $\xrightarrow{-CH_4}$ $[C_{13}H_{10}N_2Ga]^+$

279 (40.1%) 263 (6.7%)

$\xrightarrow{-Ligand}$ $[GaMe_2]^+$ $\xrightarrow{-C_2H_6}$ Ga^+

99 (19.3%) 69 (38.2%)

$\longrightarrow$ $[PhN{=}CH]^+$ $\xrightarrow{-HCN}$ $[C_6H_5]^+$ $\xrightarrow{-C_2H_2}$ $[C_4H_3]^+$

104 (15.2%) 77 (59.6%) 51 (29.3%)

$\longrightarrow$ $[PhNH_2]^+$ $\xrightarrow{-HCN}$ $[C_5H_6]^+$ $\xrightarrow{-H^{\cdot}}$ $[C_5H_5]^+$

93 (100%) 66 (1.8%) 65 (5.8%)

stability of the dimethylgallium cation in aqueous solution was noted earlier, and the peaks at m/z 99 and 101 are prominent in most of the E.I. spectra.

The mass spectra also support the conclusion that these products react with moisture. Samples of dimethylgallium-N,N′-di(p-chloro-phenyl)-acetamidine were exposed to air dried by phosphorus pentoxide and damp nitrogen, respectively. The spectrum of the former was essentially unchanged. A very interesting low temperature (less than 200°C) spectrum was obtained for the moisture reacted product. This has a totally different pattern to any other, with several series of peaks each about 100 mass units apart. The most likely explanation is that the peaks are due to Me_2Ga and MeGaO based clusters. Later spectra show a large amidine cation peak, and also some unreacted dimethylgallium amidine.

The products of the reactions between the dimethylgallium complexes and additional amidine give less satisfactory spectra. This is not entirely unexpected because they are high molecular weight species even if they are not polymeric. The only $[(amidine)_2GaMe]^+$ ion is seen in the C.I. spectrum of dimethylgallium-N,N′-dicyclohexylacetamidine, presumably due to reactions taking place in the spectrometer source. A small peak, m/z 625 due to the *bis*[N,N′-di(p-chlorophenyl)acetamidine] gallium cation occurs in the spectrum of the product of the reaction between dimethylgallium-N,N′-di(p-chlorophenyl)acetamidine and one equivalent of amidine.

The spectrum of methylgallium (N,N′-diphenylbenzamidine)(N,N′-diphenylacetamidine) contains a peak at M-18, which has not been assigned. Fast atom bombardment (F.A.B.) spectra of these compounds showed only amidine peaks. The matrix, nitrobenzylalcohol, presumably hydrolysing the products.

The mass spectrum of the gallium(III) chloride-N,N′-di(p-chloro-phenyl)acetamidine shows a cluster of small peaks around m/z 418 which supports the hypothesis that one mole of hydrogen chloride is lost at high

temperatures to give a dichlorogallium-amidine complex. Again, F.A.B. spectra showed only the amidine to be present.

X-Ray Crystallographic Studies

In order to define the structural parameters of the dimethylgallium compounds more closely, several attempts were made to obtain crystal structure data. Although the crude reaction products were usually crystalline materials, growing crystals suitable for X-ray diffraction proved difficult, however. Because the dimethylgallium derivatives are more soluble in non-co-ordinating solvents than their parent amidines, layering methods could not be used. Slow evaporation was therefore the method of choice. Unfortunately, it was found that solutions of the dimethylgallium-amidines in hydrocarbon solvents are, over a period of time, very moisture-sensitive. Good quality crystals of the free amidine form readily and on two occasions these were mounted in Lindemann tubes under nitrogen and X-ray studies undertaken. The structures of N,N′-diphenylbenzamidine and N,N′-di(p-tolyl) benzamidine were thus determined and the latter is included in Appendix 3 for completeness. The structure of N,N′-diphenylbenzamidine had been determined previously[211] so the literature results are used in the following discussion. Suitable crystals of the dimethylgallium complex with this ligand were eventually obtained by cooling the original reaction mixture, containing *n*-hexane as solvent, to -35°C for three days. After removal of the supernatant liquid at that temperature, using a syringe, the crystals were taken into a nitrogen-filled glove box and sealed into Lindemann tubes containing a small quantity of Apiezon grease to support the crystal.

Analysis of the X-ray data leads to the structure shown in Figures 7 and 8. The compound is monomeric, which contrasts with the only previously known dimethylgallium complex with a simple amidine, N,N′-dimethylacetamidine, which is dimeric (Figure 11). The unusual di-amidine, N,N′,N‴,N⁗-

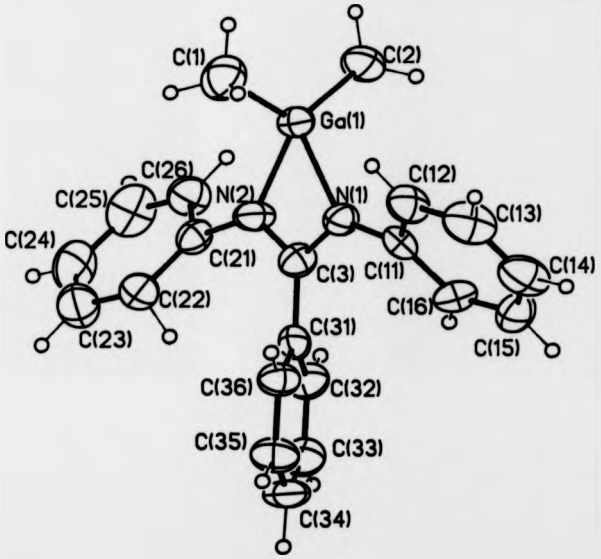


Figure 7. The molecular structure of dimethylgallium-N,N′diphenylbenzamidine, as determined by a single crystal X-ray diffraction study.

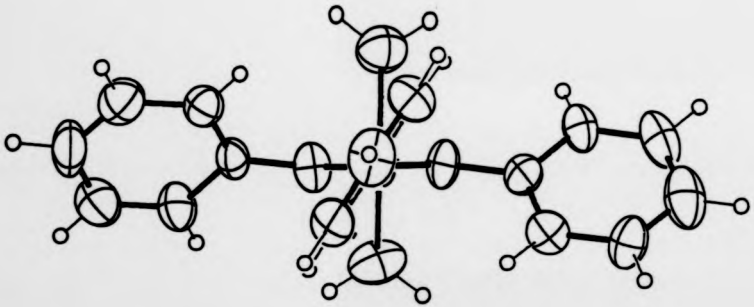


Figure 8. Another view of the molecular structure of dimethylgallium-N,N′-diphenylbenzamidine.

tetramethyloxamidine, $[MeN{=}CN(H)Me]_2$, reacts with two moles of Me_3M (M = Al, Ga, In) to give a monomeric derivative, but the gallium co-ordination environment of this interesting compound is fundamentally different, as will be shown later.

Comparison of the structures of $[Me_2Ga(PhN)_2CPh]$ and $[PhN(H)C(Ph)NPh]$.

a) Ligand Structure

As mentioned above, the solid state structure of the ligand, N,N′-diphenylbenzamidine has been determined,[211] consequently the ligand and its complex can be compared directly. The important bond lengths and angles of both compounds are shown in Figures 9 and 10. The amidine is an asymmetric dimer, with a single N-H···N bond (2.46(5)Å) so the values of bond lengths and angles shown on the relevant structures are averages, and the atom numbering scheme is omitted. The amidine has an overall propeller-like conformation. The N-C-NH unit is asymmetric, the carbon-nitrogen bonds being clearly differentiated into amine (1.360Å, average) and imine (1.303Å average). This has been found to be the case for other amidines from this work and that of other groups.[211] The mean N-C-N bond angle is 121.6°, which is again close to that of other amidines.

The structure of the dimethylgallium derivative shows several significant differences. The most important of these is the increased delocalisation over the N-C-N framework, the C-N bond lengths now being essentially equal, average 1.333Å. the bond angles also reflect this greater symmetry. The N-C-N angle of 110.8(7)Å is similar to that in transition metal complexes *(e.g. bis*(N,N′-diphenylbenzamidine)-platinum) where this ligand has adopted a bidentate chelating bonding mode.[211]

The central carbon-nitrogen bond lengths in the dimeric dimethylgallium-N,N′-dimethylacetamidine are conspicuously close to

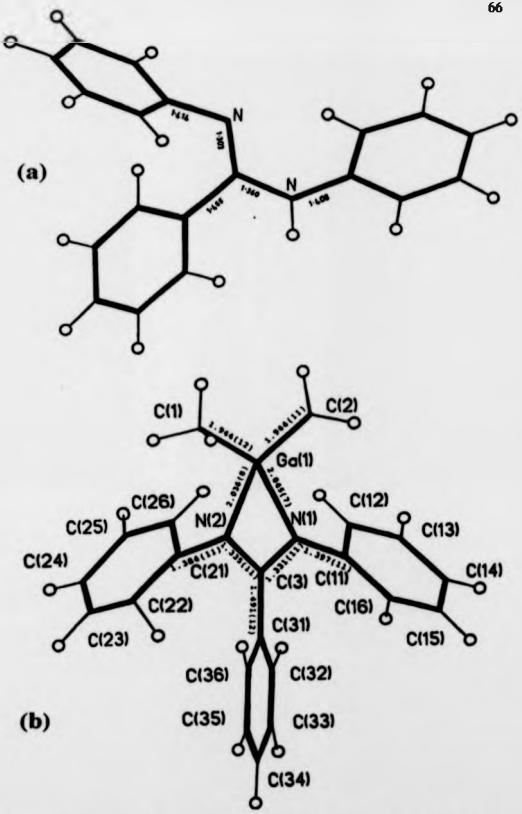


Figure 9. Comparision of the principal bond lepgths of (a) N,N′-diphenylbenzamidine and (b) dimethylgallium-N,N′-diphenylbenzamidine.

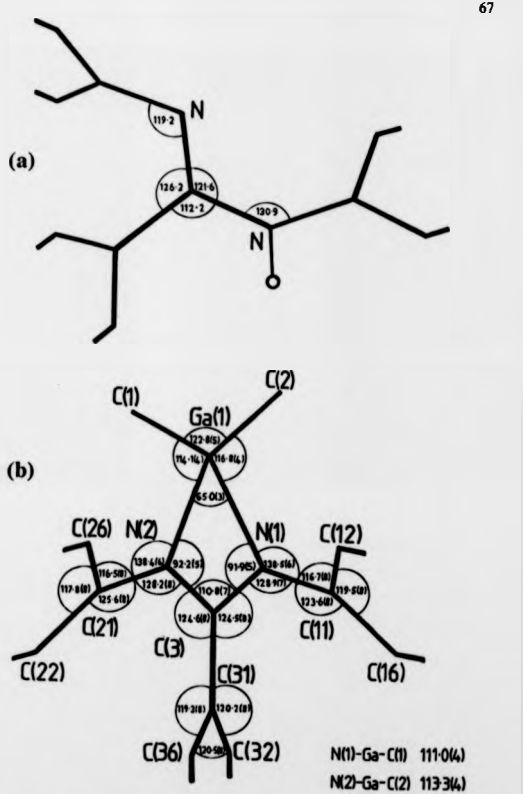


Figure 10. Comparison of the principal bond angles in (a) N,N′-diphenylbenzamidine and (b) dimethylgallium-N,N′-diphenylbenzamidine.

those in the present structure.[170] It is also notable that the N-C-N bond angle in that complex, 117.4(4)°, is much as would be expected for N,N′-diphenylbenzamidine-transition metal complexes where the amidine acts as a bridging ligand.[211] The structure is shown in Figure 11(a) and 12(a).

The structure of *bis*(dimethylgallium)-N,N′,N″,N‴-tetramethyl oxamidine (Figures 11(b) and 12(b)) is not directly comparable, because each gallium atom is co-ordinated to one nitrogen atom from each amidine moiety, forming a five membered ring.[171] This would perhaps be described as being structurally intermediate between a monomer and a dimer. This arrangement results in a very large amidine N-C-N angle of 131.6(11)°.

There is still very little crystallographic data on dimethylgallium derivatives of isoelectronic ligands to compare with these amidine complexes. Dimethylgallium-acetate and -N′-methylacetamide are known and are believed to be dimeric in solution[204] while dimethylgallium-1,3-diphenyltriazene is probably monomeric[172] but the solid state structures have not been determined, which represents a serious gap in our knowledge. Dimethylgallium-N-phenylbenzamide [(PhNC(Ph)(O)GaMe$_2$] would be worth preparing, since it could be mono- or dimeric. The aluminium compound is dimeric[212]. *Bis*(dimethylgallium)oxalate and the *cis* and *trans* N,N′-dimethyloxamide equivalents have a similar structure to the oxamidine derivative.[203,213] It was noted in Chapter 1 that there is more information available on dimethylindium complexes with carboxylates and related ligands such as thiocarboxylates, but the larger size of indium and resulting tendency to be five or six co-ordinate means that a comparison of bond lengths and even angles is likely to be of limited value. For example, in the oxamidine derivative the N-In-N bond angle is 76.0(2)°, compared with 84.0(4) for the gallium equivalent, and 85.7(1)° for aluminium.

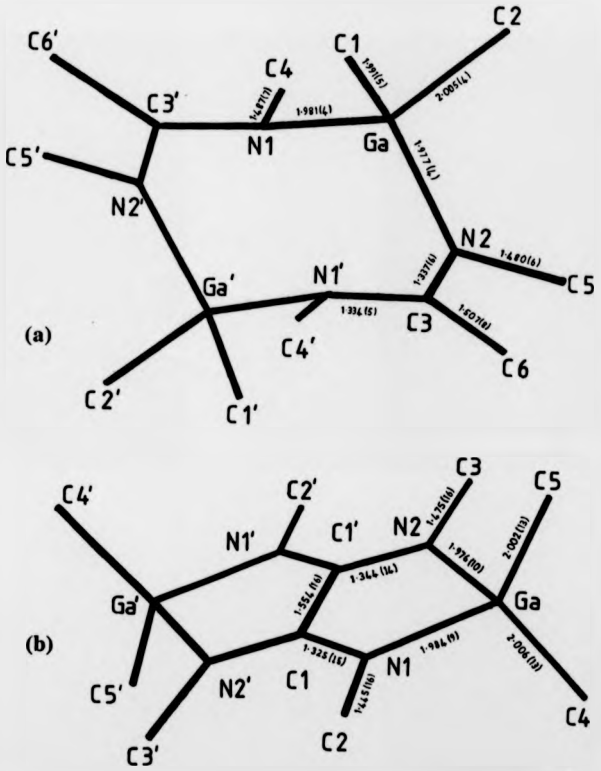


Figure 11. Comparison of the principle bond lengths of (a) dimethylgallium-N,N'-dimethylacetamidine dimer and (b) bis(dimethylgallium)-N,N',N'',N'''-tetramethyloxamidine.

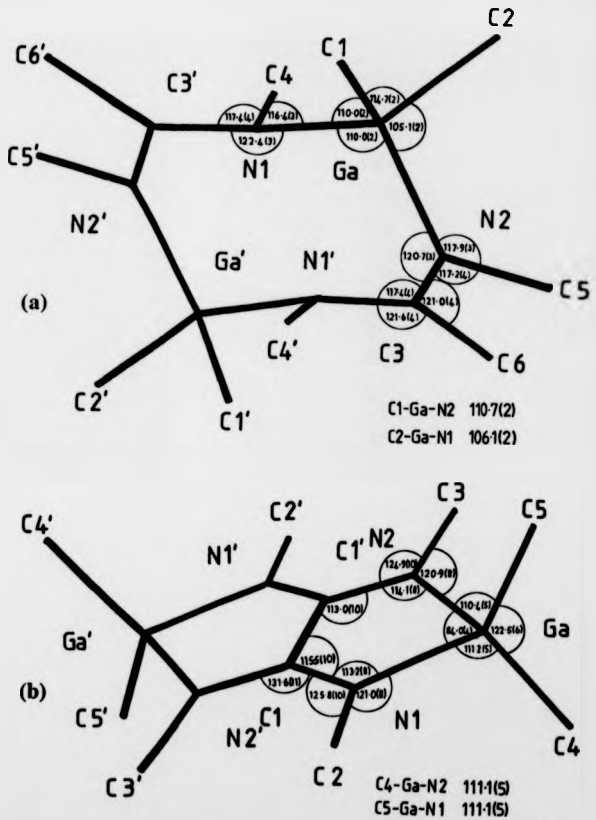


Figure 12. Comparison of the principal bond angles in (a) dimethylgallium-N,N′-dimethylacetamidine dimer and (b) bis(dimethylgallium)-N,N′,N″,N‴-tetramethyloxamidine.

b) The Gallium Co-ordination Environment

In all three dimethylgallium-amidine complexes the gallium atom is in a distorted tetrahedral environment. The gallium-carbon and gallium nitrogen bond lengths and angles are summarised in Table 6.

The gallium atom in the N,N'-dimethylacetamidine compound shows the least distortion from a perfect tetrahedron. The gallium-carbon bond lengths, average 1.998Å, are slightly longer than in gaseous trimethylgallium (1.967(2)Å)[214] and identical to those in Me_3GaNMe_3.[215] The gallium-nitrogen bonds are fractionally shorter (mean, 1.979Å). Both the Ga-C and Ga-N bond lengths obtained for the oxamidine derivative are not significantly different to those in the previous compound. However, the bond angles are more distorted. The N-Ga-N angle, as part of a five-membered ring, is only 84.0(4)° and the C-Ga-C angle has consequently increased to 122.5(6)°.

Dimethylgallium-N,N'-diphenylbenzamidine is significantly different from these two compounds, presumably due to the strain inherent in the CN_2Ga four-membered ring. The gallium-carbon bond length has decreased to 1.944Å, shorter than the gallium nitrogen bonds (mean, 2.041Å). In comparison with values summarised by Tuck,[2a] the Ga-C bonds are amongst the shortest reported for a dimethylgallium compound and the Ga-N bonds are longer than average. In this complex the N-Ga-N angle has further decreased, to 65.0(3)°, while the C-Ga-C angle is essentially the same as in the oxamidine derivative. These structural changes are also clearly illustrated by the bond angles between the amidine central carbon, nitrogen and gallium atoms. These average 121.6°, 113.7° and 92.1° for the acetamidine, oxamidine and benzamidine derivatives respectively.

Table 6 Gallium-Carbon and Gallium-Nitrogen Bond Lengths and Angles in Dimethylgallium-Amidine Complexes

	Bond Lengths (°)		Bond Angles (°)				
Compound	Ga - C	Ga - N	C - Ga - C	C - Ga - N	N - Ga - N	C···N - Ga	Ref.
Dimethylgallium-N,N′-dimethylacetamidine	1.991(5) 2.005(4)	1.981(4) 1.977(4)	114.7(2)	110.0(2) 105.1(2) 110.7(2) 106.1(2)	110.0(2)	122.4(3) 120.7(3)	170
(Mean value)	(1.998)	(1.979)	(114.7(2)	(108.0)	(110.0(2))	(121.6)	
Bis(dimethylgallium)-N,N′, N″N‴-tetramethyl-oxamidine	2.002(13) 2.006(13)	1.976(10) 1.984(9)	122.5(6)	110.4(5) 111.2(5) 111.1(5) 111.1(5)	84.0(4)	114.1(8) 113.2(8)	171
(Mean value)	(2.004)	(1.980)	(122.5(6))	(111.0)	(84.0(4))	(113.7)	
Dimethylgallium-N,N′-diphenylbenzamidine	1.944(12) 1.944(11)	2.036(8) 2.045(7)	122.8(5)	114.1(4) 116.8(4) 111.0(4) 113.3(4)	65.0(3)	92.2(5) 91.9(5)	This thesis
(Mean value)	(1.944)	(2.041)	(122.8(5))	(113.8)	(65.0(3))	(92.1)	

CHAPTER 3

Two New Organogallium-Macrocycle Complexes

CHAPTER 3 Two New Organogallium-Macrocycle Complexes

Introduction

It was noted in Chapter 1 that the interaction of organogallium compounds with macrocyclic ligands is a rather recent field of study. This is surprising because derivatives formed are of interest because of the unusual stereochemistry which might be imposed on the gallium centre, and the possible use of such compounds as photoactive polymerisation catalysts. The latter relates to the use of related porphyrin derivatives of aluminium alkyls, following the work of Inoue *et al*,[216] as catalysts for the polymerisation of methacrylates, and other similar compounds.

The first crown ether adduct of trimethylgallium was prepared by Robinson and co-workers in 1987.[217] In 1990 the same group reported the first organogallium complexes with macrocyclic tetradentate amines.[218] The presently known organogallium macrocyclic complexes (excluding the porphyrin derivatives[177-179]) are shown, in Table 1, in the order in which they were reported.

The structures are illustrated in Figure 1.

Table 1. Published organogallium-macrocyclic complexes

	Compound	Formula	Ref
I	$(Me_3Ga)_2$[dibenzo-18-crown-6]	$C_{26}H_{42}O_6Ga_2$	217
II	(Me_2Ga)[4,13 diaza-18-crown-6]$(GaMe_3)_2$	$C_{20}H_{49}N_2O_4Ga_3$	219
III	$(Me_3Ga)_4$[Me_4[14]aneN_4]	$C_{26}H_{69}N_4Ga_4$	218
IV	$(MeGa)_2$[14]ane$N_4(GaMe_3)_2$	$C_{18}H_{44}N_4Ga_4$	218
V	$(Me_3Ga)_2$[14]aneN_4	$C_{10}H_{42}N_4Ga_2$	220
VI	$(MeAl)_2$[14]ane$N_4(GaMe_3)_2$	$C_{18}H_{44}N_4Al_2Ga_2$	220

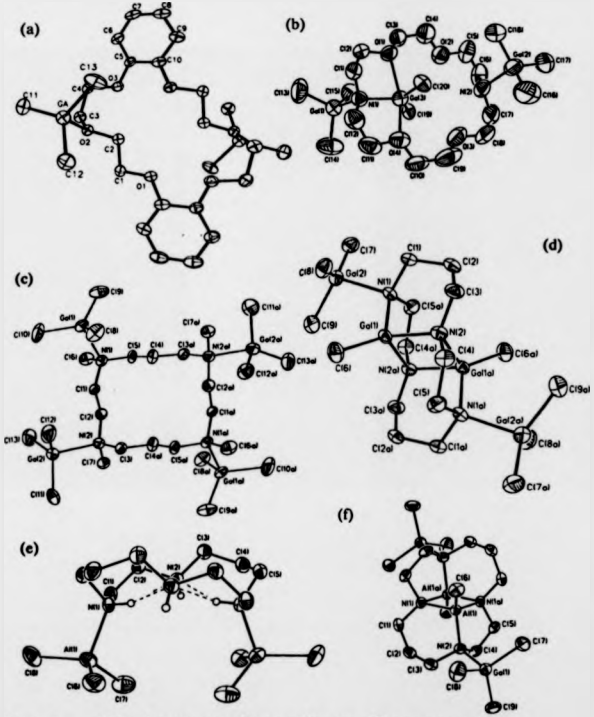


Figure 1. Molecular structures of reported organogallium - macrocycle complexes

(a) $(Me_3Ga)_2$ [dibenzo-18-crown-6].[217]

(b) (Me_2Ga)[4,13-diaza-18-crown-6]$(GaMe_3)_2$.[219]

(c) $(Me_3Ga)_4[Me_4[14]aneN_4]$.[218]

(d) $(MeGa)_2$[14]$aneN_4(GaMe_3)_2$.[218]

(e) $(Me_3Al)_2$[14]$aneN_4$. The equivalent gallium compound is isostructural.[220]

(f) $(MeAl)_2$[14]$aneN_4(GaMe_3)_2$.[220]

In view of this paucity of relevant literature, it was decided to investigate the reactions of trimethylgallium with 5,7,12,14-tetramethyldibenzo [b,i][1,4,8,11] tetraazacyclotetradecine, usually abbreviated H_2tmtaa. This macrocycle was chosen for several reasons. The reaction between H_2tmtaa and triethylaluminium has been studied,[221] allowing comparisons to be made between the gallium and aluminium compounds. The Al-Et bond in EtAltmtaa is photosensitive. This macrocycle is also of interest because it has a conjugated ring system which makes it intermediate between completely aliphatic macrocycles such as [14]aneN_4 ("cyclam") and the aromatic porphyrin systems. It is much more rigid than the aliphatic macrocycles. In the unsaturated nature of the NH proton system it is also reminiscent of the amidine complexes reported in Chapter 2. Finally, this macrocycle is relatively easy to prepare in quantity. This chapter describes the preparation, molecular structure and spectroscopic properties of the two new organogallium compounds produced.

Preparation of the Complexes

Evidence described in the remainder of this chapter shows that H_2tmtaa reacts with trimethylgallium in n-hexane at or below room temperature to eliminate one mole of methane to form the dimethylgallium compound $[(C_{22}H_{23}N_4)GaMe_2]$. This yellow solid exhibits considerable thermal stability - only negligible decomposition occurs after 5 hours at 160°C, but on further heating the powder turns red just prior to melting at about 225°C. The thermogravimetric analysis (T.G.A.) and differential thermal analysis (D.T.A.) plots for $[(C_{22}H_{23}N_4)(GaMe_2)]$ are reproduced in Figure 2. They show the initial melting and methane elimination reaction (225°C) with complete decomposition or vaporisation occurring around 330°C.

The red product is the monomethylgallium derivative, $[(C_{22}H_{22}N_4)GaMe]$. This reaction sequence is essentially the same as that for the reported ethyl aluminium compound,[221] although that compound evolves a

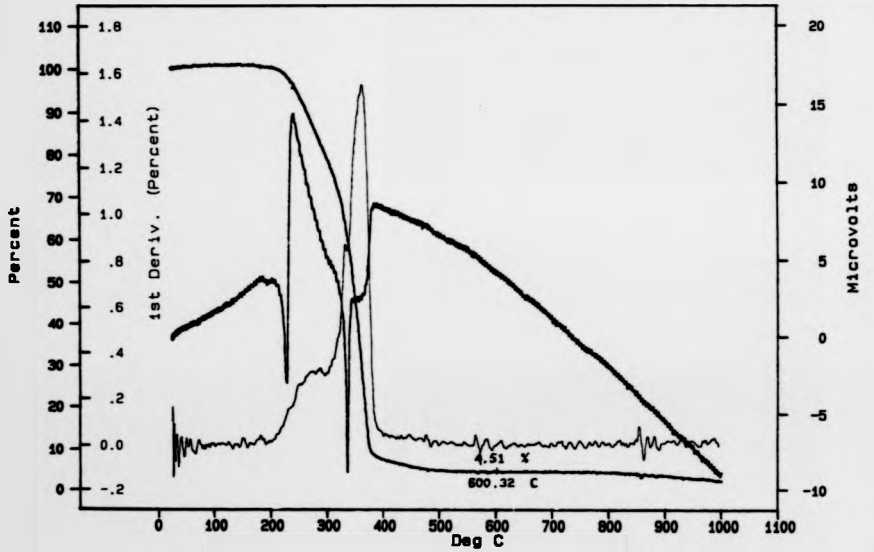


Figure 2. Combined T.G.A. and D.T.A. plot for $Me_2GaHtmtaa$.

second mole of ethane at only 100°C, which is consistent with the typically greater reactivity of aluminium-carbon bonds. Indeed, as noted in that report, the thermal stability of the monoethyl-aluminium compound, which is not decomposed at 300°C, is remarkable. It is also surprisingly stable to attack by protic reagents, as mentioned earlier, but the AlEt bond is photosensitive. The chemical reactivity of the gallium compounds has not yet been explored, but they do not appear to be light sensitive and they are not obviously air sensitive.

The fact that the initial alkane elimination reaction occurs at room temperature with Me_3Ga, as it does with the amidine ligands discussed in Chapter 2, is consistent with the greater acidity expected of the NH proton in a potentially delocalised system. In contrast, reactions with secondary amines such as Ph_2NH and cyclam, normally require elevated temperatures, often about 100°C, to react with trimethylgallium.[46, 218] The cyclam reaction is particularly interesting. No alkane elimination occurs with two equivalents of MMe_3 (M = Al, Ga) at room temperature,[220] but after 24 hours at 130°C, in the presence of four equivalents of trimethylgallium, all four NH groups react to yield $[(MeGa)_2[14]aneN_4(GaMe_3)_2]$[218] rather than $[(Me_2Ga)_4[14]aneN_4]$, presumably the conformation of the intermediates favours intramolecular elimination reactions. The reaction with diaza-18-crown-6 and excess trimethyl gallium under the same conditions follows the usual pattern and only one mole of methane is evolved (Figure 1b).[219] It therefore resembles $Me_2GaHtmtaa$ in having an unreacted NH group, even though in this case two trimethylgallium molecules are co-ordinated to the nitrogen lone pairs. $Me_2GaHtmtaa$ does not co-ordinate or react with excess trimethylgallium. This is probably explained in part by the inaccessibility of the nitrogen lone pairs and the remaining NH proton, because these are pointing approximately towards the dimethylgallium unit, but as they are too distant to co-ordinate they may be partially shielded by it on one side. It is also likely that the acidity of the NH proton is reduced by inductive effects.

Spectroscopic Properties

N.M.R. Spectra

The ^{1}H and ^{13}C N.M.R. spectra are consistent with the results of the X-ray crystallographic studies, discussed later, and they provide a very clear example of the effect of molecular symmetry on N.M.R. spectra. The ^{1}H and ^{13}C spectra of H_2tmtaa, Me_2GaHtmtaa and MeGatmtaa are illustrated in Figure 3 and Figure 4 respectively. The resonances are listed and assigned in Tables 2 and 3.

Table 2. Summary of ^{1}H N.M.R. data (400 MHz) for H_2tmtaa, Me_2GaHtmtaa and MeGatmtaa. Integrals are in parenthesis, reference is $SiMe_4$ = 0.

Compound	δ (p.p.m.)				
	NH	ArH	CH	CH_3	Ga-CH_3
H_2tmtaa	13.57(2H)	6.98(8H)	4.87(2H)	2.13(12H)	-
Me_2GaHtmtaa	12.43(1H)	6.98 - 7.13(8H)	4.96(1H)	1.64(6H)	-0.38(3H)
			4.79(1H)	2.09(6H)	-1.15(3H)
MeGatmtaa	-	6.97 - 7.07(8H)	4.80(2H)	2.21(12H)	-0.93(3H)

Figure 3 ^1H N.M.R. spectra of (a) MeGatmtaa, (b) Me_2GaHtmtaa (c) H_2tmtaa.

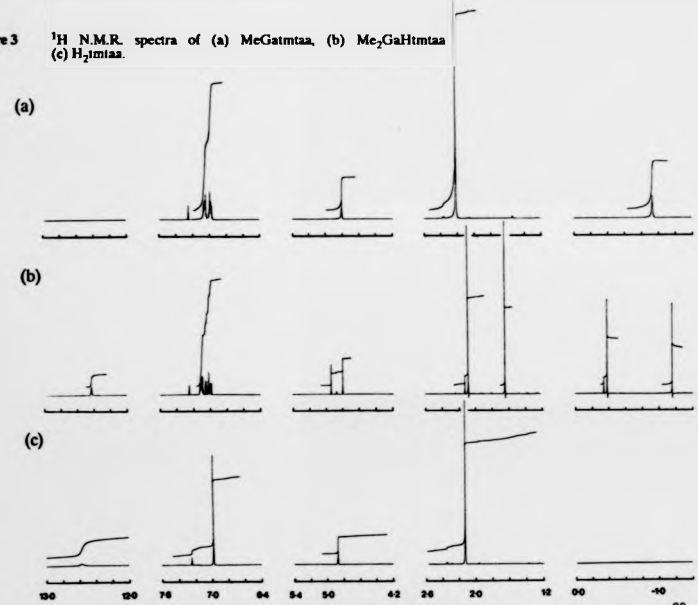


Figure 4 ^{13}C N.M.R. spectra of (a) MeGatmtaa, (b) $Me_2GaHtmtaa$ (c) H_2tmtaa.

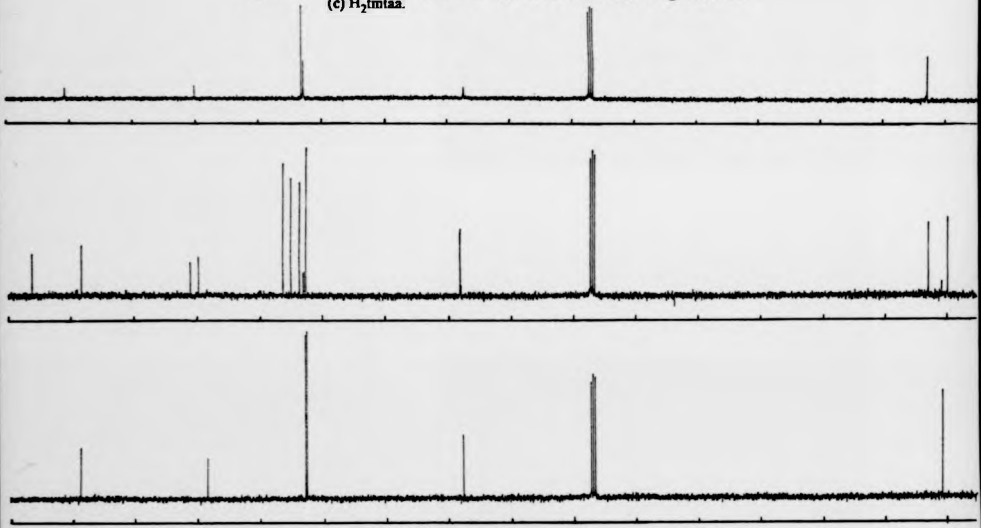


Table 3 Summary of ^{13}C N.M.R. data (400 MHz) for H_2tmtaa, Me_2GaHtmtaa and MeGatmtaa (rel. $SiMe_4$ = 0)

δ(p.p.m.)			
H_2tmtaa	Me_2GaHtmtaa	MeGatmtaa	Postulated assignments
158.8372	166.13	160.69	C---N
	158.17		
138.3775	140.95	139.98	ArN
	139.69		
123.0007	126.20	123.01	ArH
122.7886	124.94	122.72	
	123.60		
	122.56		
97.8390	98.02	97.28	methine CH
	97.95		
20.8059	22.97	22.91	CH_3
	19.84		

The ^1H spectrum of the dimethylgallium derivative shows a single broad resonance at 12.43 p.p.m., with relative integral one, due to the remaining NH proton, but the aromatic region is complex. The fact that all the other resonances consist of pairs of singlets, including two inequivalent sets of Ga-CH_3 groups, indicates that the position and orientation of the dimethylgallium unit in $CDCl_3$ solution is probably the same or very similar to that in the solid state. Traces of an unidentified species (~5%) can also be seen in both the ^1H and ^{13}C spectra of this compound.

The spectrum of the monomethyl-gallium compound shows that the symmetry of the molecule has increased, so that the spectrum resembles that of

the free ligand except for the lack of an NH resonance. The gallium derivative does show also a more complex aromatic region, and as expected, the presence of the single Ga-CH_3 resonance at -0.93 p.p.m. This implies that the gallium atom is in a central position with the gallium methyl group in a symmetrical axial position or in rapid rotation.

The same basic pattern is repeated in the more complex ^{13}C spectra. The most interesting feature is the absence of resonances due to the gallium-methyl carbon atoms, which were expected to be visible at about 0 p.p.m. At present we have no convincing explanation for this observation. These spectra are shown in Figure 4.

Infra-Red Spectra

Infra-red spectra have been obtained of Nujol mulls of H_2tmtaa, Me_2GaHtmtaa and MeGatmtaa, and the significant peaks are listed in the experimental section. The spectra are complex and have not been assigned in detail, but several points are worthy of note. The NH bands of the free ligand and the dimethylgallium derivative, expected at about 3300 cm^{-1} were not detected, probably because of hydrogen-bonding involving the nitrogen atoms. Secondly, the spectrum of Me_2GaHtmtaa is generally more complex than those of H_2tmtaa and MeGatmtaa, presumably due to the reduced symmetry of the molecule. The most distinctive feature of the spectrum of MeGatmtaa is that it has no bands in the "fingerprint region" at a higher frequency than 1572 cm^{-1}, whilst both the free macrocycle and the dimethyl gallium complex both have prominent peaks close to 1620 and 1590 cm^{-1}. It is likely that these are C=N stretching frequencies, and they are shifted to lower wavenumbers in MeGatmtaa as a result of increased π delocalisation in that complex. Spectra of both gallium derivatives contain low frequency bands that are probably at Ga-C stretching frequencies. Those for Me_2GaHtmtaa occur at 575 and 535 cm^{-1}, those for MeGatmtaa at 565 and 522 cm^{-1}.

Mass Spectra

The mass spectra of the compounds are useful, not only for providing positive evidence of the identify of the compounds, but also for showing how readily $Me_2GaHtmtaa$ is thermally decomposed to MeGatmtaa. The important high mass peaks of the E.I. spectra of the ligand and both gallium compounds are given in Table 4 below:-

Table 4. Summary of the E.I. Mass Spectra of H_2tmtaa, $Me_2GaHtmtaa$ and MeGatmtaa

Compound	m/z	Relative intensity(%)	Assignment*
H_2tmtaa	344	24.4	M^+
	343	100.0	$(M-H)^+$
	328	74.0	$(M+H-CH_3)^+$
$Me_2GaHtmtaa$	443	2.9	$(M+H)^+$
	442	1.4	M^+
	427	94.3	$(M+H-CH_4)^+$
	411	100.0	$(M+H-2CH_4)^+$
MeGatmtaa	427	56.3	$(M+H)^+$
	426	37.4	M^+
	411	100.0	$(M+H-CH_4)^+$

* M is the molecular ion of the appropriate compound . Equivalent ^{71}Ga peaks neglected.

In all cases proton migration reactions have occurred, the major ions actually being part of a group, each member separated by one mass unit. Ions corresponding exactly to the expected decomposition products are not usually the most intense.

The low intensity of the molecular ion of the dimethylgallium derivative is unsurprising - at the temperature required to volatalise the sample this compound is clearly decomposing into the monomethyl compound.

Numerous lower mass fragments arising from the rupture of the macrocyclic ring at various points are also observed, particularly in the spectrum of the neutral ligand, which contains prominent peaks due to the ions m/z 211 (16.6%), 197 (55.5%), 172 (32.3%), 157 (20.0%) 133 (35.6%).

Ga^+ (m/z 69,71) is prominent in the mass spectra of both $Me_2GaHtmtaa$ and MeGatmtaa (15.1% and 32.3%, respectively) but $MeGa^+$ (m/z 84,86) and Me_2Ga^+ (m/z 99,101) are not significant.

X-Ray Crystallographic Studies

Single crystal X-ray diffraction studies have been conducted on both compounds reported in this chapter. The labeling scheme and the interatomic distances of the neutral H_2tmtaa ligand[222] and the di- and monomethyl-gallium derivatives are shown in Figure 5. Further views of the gallium compounds are provided in Figures 6 - 9.

The Effects of Reaction Upon Ligand Structure

The effects of complexation with transition metal ions on the solid state conformation of this ligand has been the subject of a number of investigations[222,223] and is also covered by a recent review.[224] Although we are concerned with main group chemistry, most of the features noted with transition metals are applicable here.

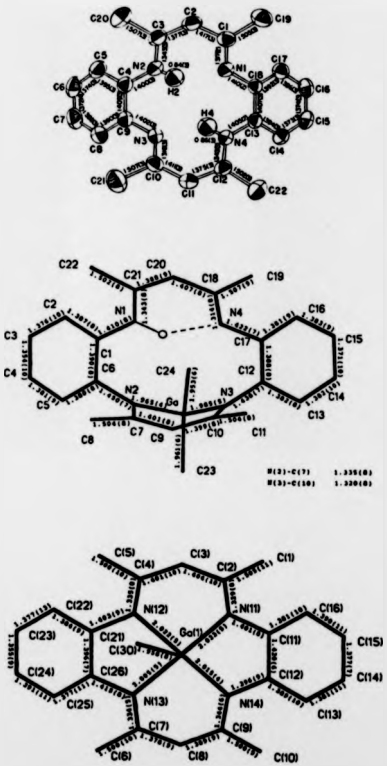


Figure 5 The molecular structures, showing bond lengths (Å) of, from top, H_2tmtaa, Me_2GaHtmtaa and MeGatmtaa.

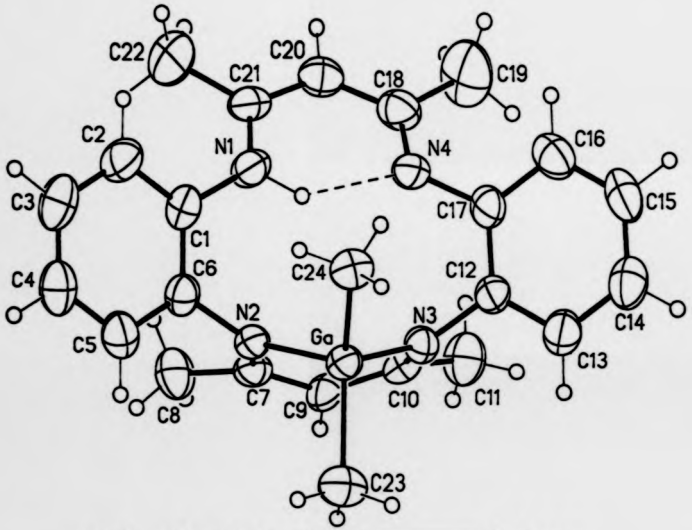


Figure 6 The molecular structure of $Me_2GaHtmtaa$, showing atom numbering scheme.

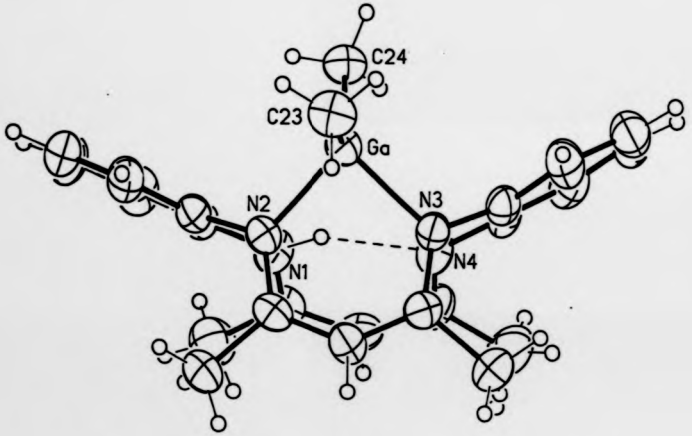


Figure 7 Another view of the structure of $Me_2GaHtmtaa$, illustrating the pronounced saddle shape of the ligand.

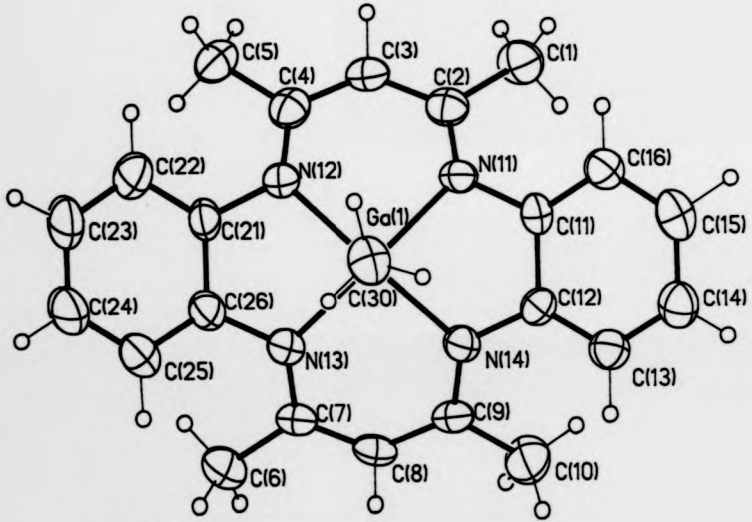


Figure 8 The molecular structure of MeGatmtaa, showing atom numbering scheme.

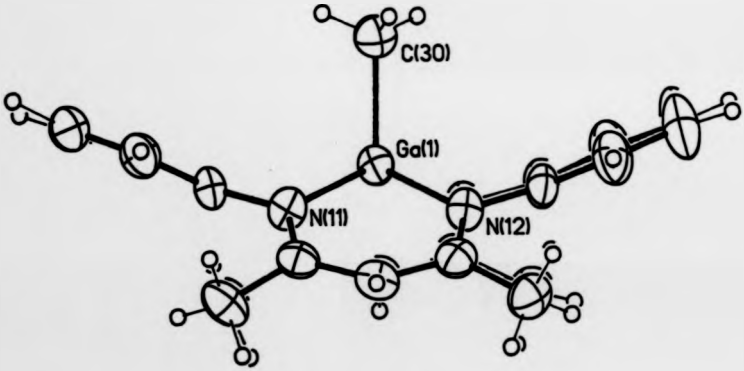


Figure 9 Another view of the structure of MeGatmtaa, again showing the saddle shape of the ligand.

The conjugated structure of this ligand causes it to be much more rigid than aliphatic macrocycles. It has features in common with the porphyrin and phthalocyanine ligands as noted earlier. The principal similarities and differences in the two systems have been summarised.[222,224] The similarities are (1) The four nitrogen atoms of H_2tmtaa are confined to a square planar configuration (2) Upon complexation with a metal ion it normally loses two protons to give a dianion (3) which has a completely conjugated system of double bonds. The differences include (1) This macrocycle has a 14 membered rather than a 16 membered ring as in porphyrins so the ideal metal-nitrogen distance is shorter. The nitrogen-centre distance is about 1.902Å for the neutral ligand[222] and probably only 1.85-1.87Å in the dianion[223] compared with about 2.01Å in porphyrins[225]. (2) Unlike porphyrins the anionic charges are not completely delocalised over the entire ligand framework, but are mainly localised in the six-membered 2,4-pentamediiminato chelate rings. (3) Although completely conjugated the π system of the dianion is an anti-aromatic (4n) and not an aromatic (4n + 2), π-electron system as in the porphyrins.

The rigid nature of the structure has several interesting, but subtle consequences. For example, it means that, unlike many aliphatic macrocycles, the conformation of the free ligand is very similar to that in the complexes, and thus justifies detailed comparisons. The most important feature is the way this ligand favours five coordinate, square-based pyramidal structures due to the pronounced saddle shape of the free ligand. This is caused by steric interactions between the methyl groups and benzenoid rings, and results in the nitrogen lone pairs pointing out of the same side of the molecule as the benzenoid rings. A metal therefore resides on that side of the N_4 plane and the axial coordination sites are therefore inequivalent. This effect increases with metal size, small metal ions such as Co(III)[223] can even flatten the conformation by pulling the lone pairs into the N_4 plane. The non-planarity of this ligand inhibits aggregation so leading to greater solubility than totally conjugated planar macrocycles such as

porphyrin, phthalocyanin and the simple dibenzo ligand.[226] A side view of the free ligand is shown in Figure 10.[222]

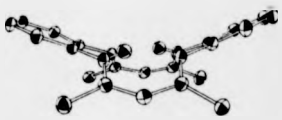


Figure 10. Side view of the neutral ligand, H_2tmtaa, showing its saddle shape.

It can be seen from Figure 5 that the structures of the gallium compounds are similar to those reported and postulated, for the mono- and diethylaluminium derivatives respectively.[221] The main features to note are that, as expected,[222,223] deprotonation leads to increased conjugation over the 2,4-pentanediiminato unit involved, which is expressed as an equalisation of the relevant bond lengths. This is clearly seen in the dimethylgallium macrocycle, where the difference between formally single (C(21)-N(1)) and double (C(18)-N(4)) C-N bonds is 0.029Å in the protonated NCCCN moiety, but only 0.015Å between the N(2)-C(7) and N(3)-C(10) bonds in the chelate ring bonded to the organogallium unit. This compares with equivalent differences of 0.026Å and 0.027Å within each NCCN unit in the free H_2tmtaa ligand, and almost negligible variations of 0.006Å and 0.010Å in MeGatmtaa (see Figure 5). The benzenoid carbon to nitrogen bonds have an important role in compensating for structural changes that occur on complexation because, having the greatest amount of single bond character, they are the most easily deformed. In Me_2GaHtmtaa these bonds are considerably lengthened from an average of 1.404Å in both the free ligand and the monomethyl gallium compound to 1.430Å (C(1)-N(1)

= 1.410Å and C(17)-N(4) = 1.422Å at the protonated side of the molecule, C(12)-N(3) = 1.438Å and C(6)-N(2) = 1.450Å where the gallium is co-ordinated). Bond angles are also distorted. Table 5 shows the C-N-C bond angles for the ligand and both gallium compounds.

Table 5 C-N-C Bond Angles (°) in H_2tmtaa, Me_2GaHtmaa and MeGatmtaa

H_2tmtaa		Me_2GaHtmtaa		MeGatmtaa	
Bond	Angle(°)	Bond	Angle(°)	Bond	Angle(°)
C(3)-N(2)-C(4)	129.1(2)	C(1)-N(1)-C(21)	127.8(5)	C(4)-N(12)-C(21)	124.8(6)
C(1)-N(1)-C(18)	125.7(2)	C(17)-N(4)-C(18)	125.7(5)	C(2)-N(11)-C(11)	125.1(6)
C(9)-N(3)-C(10)	125.1(2)	C(6)-N(2)-C(7)	120.3(4)	C(7)-N(13)-C(26)	124.6(6)
C(12)-N(4)-C(13)	129.8(2)	C(10)-N(3)-C(12)	124.5(5)	C(9)-N(14)-C(12)	124.5(5)

Most of these angles are near to 120°, as might be expected. The largest, close to 130°, involve the nitrogen atoms bearing a proton. In Me_2GaHtmtaa it can be seen that the angles C(6)-N(2)-C(7) and C(10)-N(3)-C(12) are decreased to 120.3° and 124.5° respectively, the nitrogen atoms presumably being pulled together by the dimethylgallium group. In MeGatmtaa all the nitrogen atoms are being pulled towards the centre of the macrocyclic ring, and, as Table 5 shows, all four C-N-C bond angles are close to 125°.

The Co-ordination Environment of the Gallium Atoms

The important gallium bond angles are listed in Table 6.

Table 6. Significant bond angles at Gallium in $Me_2GaHtmtaa$ and MeGatmtaa

$Me_2GaHtmtaa$		MeGatmtaa	
Bond	**Angle(°)**	**Bond**	**Angle(°)**
N(2)-Ga-N(3)	90.7(2)	N(11)-Ga(1)-N(12)	89.6(2)
N(3)-Ga-C(23)	110.1(2)	N(12)-Ga(1)-N(13)	78.7(2)
		N(12)-Ga(1)-N(14)	141.4(2)
N(3)-Ga-C(24)	110.0(2)	N(11)-Ga(1)-C(30)	108.6(3)
N(2)-Ga-C(23)	107.8(2)	N(13)-Ga(1)-C(30)	107.7(3)
		N(11)-Ga(1)-N(13)	143.8(2)
N(2)-Ga-C(24)	108.8(2)	N(11)-Ga(1)-N(14)	78.8(2)
C(23)-Ga-C(24)	124.3(3)	N(13)-Ga(1)-N(14)	89.3(2)
		N(12)-Ga(1)-C(30)	108.2(2)
		N(14)-Ga(1)-C(30)	110.4(3)

The gallium co-ordination geometries are illustrated in Figure 11.

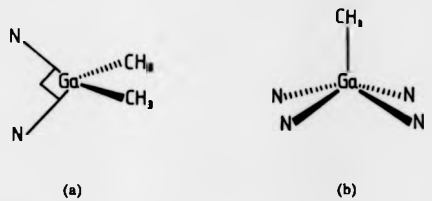


Figure 11. The co-ordination geometry of gallium in (a) $Me_2GaHtmtaa$ and (b) MeGatmtaa

In $Me_2GaHtmtaa$ the metal atom is in a distorted tetrahedral environment, C_2GaN_2, with the methyl carbon atoms separated by 124.3°, the nitrogen atoms by 90.7°. The N_4GaCH_3 unit in MeGatmtaa forms a distorted square-based pyramid . The gallium atom is 0.65Å above the N_4 plane and the nitrogen-centre distance is 1.908Å. This compares with 0.57Å and 1.88Å respectively for the aluminium compound,[221] and is within the ranges of 0.24-0.73Å and 1.893 - 1.988Å found for the respective parameters in the cobalt(III), iron(III) and manganese(II) complexes with this ligand. The out-of-plane displacements of the gallium and aluminium atoms are significant as they are approximately half the covalent radius of these metals.

The gallium co-ordination geometries in these compounds, although much as would be expected, are thus significantly different from any of the other reported organogallium macrocyclic complexes. The compound $Me_2Ga(C_{12}H_{25}N_2O_4)(GaMe_3)$ is the only other example containing a dimethylgallium unit, but that gallium atom is in an unusual C_2GaNO_2 trigonal-

bipyramidal environment with an O-Ga-O bond angle of 157° as illustrated previously in Figure 1 and in Figure 12, below.

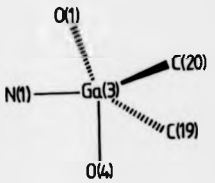


Figure 12. The co-ordination geometry of the Dimethylgallium unit in $Me_2Ga(C_{12}H_{25}N_2O_4)(GaMe_3)_2$

Relevant bond angles(°) are O(1)-Ga(3)-O(4), 157.2(2), C(19)-Ga(3)-C(20), 135.1(9), N(1)-Ga(3)-C(19), 112.2(6), N(1)-Ga(3)-C(20), 112.6(7), O(1)-Ga(3)-C(19), 102.4(7), O(1)-Ga(3)-C(20), 86.5(7), O(4)-Ga(3)-C(19), 98.0(7), O(4)-Ga(3)-C(20), 86.2(7), N(1)-Ga(3)-O(1), 78.5(3), O(4)-Ga(3)-N(1), 84.5(2).

The trimethylgallium moieties in this compound and the various organogallium species in the other previously published macrocyclic complexes all exhibit distorted tetrahedral coordination with C_3GaO, C_3GaN and $CGaN_3$ units in the various compounds.[217-220]

The principal bond lengths of the reported organogallium macrocyclic complexes are summarised in Table 7.

Table 7. Important Bond Lengths in Organogallium-Macrocyclic Complexes

Compound	Gallium fragment	d(Ga-C) (Å)	d(Ga-N) (Å)	d(Ga-O) (Å)	Ref
$(GaMe_3)_2(C_{20}H_{24}O_6)$	$GaMe_3$	2.00(1) 1.99(1) 2.01(1)	-	2.198	217
$GaMe_2(C_{12}H_{25}N_2O_4)(GaMe_3)_2$	$GaMe_2$	1.95(2) 1.97(2)	2.024(5)	2.450(5) 2.278(5)	219
	$GaMe_3$	1.969(9) 1.982(9) 2.002(9) 2.007(9) 1.966(9) 1.999(8)	2.164(5) 2.171(6)		
$(GaMe_3)_4Me_4[14]aneN_4$	$GaMe_3$	1.967(5) 1.973(6) 1.963(5) 1.971(7) 1.970(6) 1.986(6)	2.182(4) 2.202(4)	-	218
$(GaMe)_2[14]aneN_4(GaMe_3)_2$	GaMe	1.933(7)	1.943(5) 2.014(6) 2.003(6)	-	218
	$GaMe_3$	1.998(8) 1.993(8) 1.994(8)	2.136(5)		
$(GaMe_3)_2[14]aneN_4$	$GaMe_3$	1.966(8) 1.94(1) 1.991(9)	2.134(4)	-	220
$(AlMe)_2[14]aneN_4(GaMe_3)_2$	$GaMe_3$	1.993(8) 1.983(5) 1.986(7)	2.136(3)	-	220
$GaMe_2(C_{22}H_{23}N_4)$	$GaMe_2$	1.953(6) 1.981(6)	1.965(4) 1.985(4)	-	This study
$GaMe(C_{22}H_{22}N_4)$	GaMe	1.958(8)	2.022(5) 2.023(5) 2.015(4) 2.005(5)	-	This study

The gallium-carbon bond lengths in both $Me_2GaHtmtaa$ and MeGatmtaa are fractionally shorter than the value of 1.967(2)Å found for gaseous trimethylgallium.[214] They are also significantly shorter than the values of 1.963(5)-2.01(1)Å found for $GaMe_3$ coordinated to macrocycles, but are within the 1.95(2) - 1.97(2)Å range found for the dimethylgallium unit in $GaMe_2(C_{12}H_{25}N_2O_4)(GaMe_3)_2$. At 1.958(8)Å the Ga-C bond in MeGatmtaa is somewhat longer than that of the monomethylgallium unit in $(GaMe)_2[14]aneN_4(GaMe_3)_2$, 0.933(7)Å, but it is shorter than the C-Al bond (1.976(3)Å) in the equivalent ethylaluminium compound.[221]

The gallium-nitrogen bond lengths in $Me_2GaHtmtaa$ are much shorter than any in $Me_2Ga(C_{12}H_{25}N_2O_4)(GaMe_3)_2$, but in the latter compound the dimethylgallium unit is five-coordinate as noted earlier (Figures 1 and 12). The difference in the Ga-N distances is less marked when compared with values published for Me_2GaL compounds, such as the oxamidine[171] complex (average 1.980Å) and $[Me_2Ga(N_2C_5H_7)]_2$ (average 1.993Å).[227] The average Ga-N bond lengths in MeGatmtaa are, at 2.016Å, much longer than the shortest monomethylgallium-nitrogen bond in $(MeGa)_2[14]aneN_4(GaMe_3)_2$ (Ga(1)-N(1) = 1.943Å) but only slightly longer than Ga(1)-N(2a) and Ga(1)-N(2) (2.003(6)Å and 2.014(6)Å) respectively. No other monomethylgallium-nitrogen bond lengths have been published for further comparisons. It can be seen that these values are significantly shorter than the Me_3Ga-N distances of 2.12 - 2.20Å recorded in Table 4.

CHAPTER 4

Some Co-ordination Compounds of Dimethylindium Iodide

CHAPTER 4 Some Co-ordination Compounds of Dimethylindium Iodide

Introduction

In this chapter are reported the results of some reactions between dimethylindium iodide (Me_2InI) and ligands containing Group 15 donor atoms. The reason for choosing to study Me_2InI is that it is easily prepared by reacting indium metal directly with methyl iodide in the absence of solvent.

$$2In + 3MeI \longrightarrow Me_3In_2I_3$$

The Me_2InI is easily obtained from the sesquiiodide by adding potassium iodide to complex the $MeInI_2$ portion of the sesquiiodide, and then subliming off the Me_2InI.[136]

$$Me_3In_2I_3 + KI \longrightarrow Me_2InI + K[MeInI_3]$$

The formation of adducts of Me_2InI with ligands containing donor atoms such as phosphorus or arsenic is of interest since such species can act as suitable precursors to the III-V semi-conductors (InP, etc.) after further alkylation to give trialkylindium adducts. This is easily achieved if required using lithium alkyl reagents,[70] so that a direct and convenient route to adducts of alkyl indium derivatives now exists.

The known co-ordination compounds of the organoindium halides are summarised in Table 1.

It can be seen that very little structural information is available, and none for ligands with Group 15 donors other than nitrogen. This stands in contrast to the much larger body of literature concerned with compounds formed between indium trialkyls and phosphines and arsines. The primary aim of this work was, therefore, to prepare some new complexes involving Me_2InI with phosphine and arsine ligands, in particular, and to investigate the structure of adducts for which suitable data could be obtained. Data on compounds involving polydentate ligands was thought likely to be of particular interest. Unfortunately, no suitable crystals could be obtained of the phosphine and arsine complexes, but the

Table 1 Neutral co-ordination compounds of the organoindium halides

Ligand	Complex	Halide (X)	Ref
Ammonia*	$Me_2InX.L$	Cl, I	158
	$Me_2InX.L_2$	Cl, I	158
	$Me_2InX.L_3$	Cl, I	158
t-Butylamine	$MeInX_2.L$	Cl†	228
Ethylenediamine	$Me_2InX.L$	Cl, I	158
TMEDA	$EtInX_2L$	Br†, I†	229
	$Cl(X)InCH_2InCl_2$	Cl†, Br†, I	162
	X_2InCH_2X 1.5L	Cl	162
Pyridine	$MeInX_2.L_2$	Cl	158
	$Me_2InX.L$	Cl, I	112
	$(PhC)_4InX.L$	Cl	161
2,2′-Bipyridine	$Me_2InX.L$	Cl, I	143, 158
	$Et_2InX.L$	I	143
	$MeInX_2.L$	Cl, I	143, 158
	$EtInX_2.L$	Br	143
	$PhInX_2.L$	Cl, Br, I	143
	$CpInX_2.L$	I	42
	$BzInX_2.L$	Cl, Br, I	143
	$C_6F_5InX_2.L$	Br	143
1,10-Phenanthroline	$Me_2InX.L$	Cl	158
	$CpInX_2.L$	I	42
2,2′,2″-Terpyridine	$MeInX_2.L$	Cl	158
Dimethylformamide	$(CF_3)_2InX$	Cl	230
Triphenylphosphine	$(Me_2InX)_2L$	Cl	112
	$Me_2InX.L$	I	112
Triphenylphosphineoxide	$Me_2InX.L$	Cl, I	158
Triphenylarsineoxide	$Me_2InX.L$	Cl	158
Trimethylstibinesulphide	$Me_2InX.L$	Cl	231
	$MeInX_2.L$	Cl	231
	$Et_2InX.L$	Cl, Br	231
1,4-Dioxane	$(Allyl)InX_2.L$	Br, I	232
	$BzInX_2.L$	Br, I	232
Dimethylsulphoxide	$X_2InCH_2X.L$	Br	162

* Identified from tensimetric studies.
† Crystal structure determined

molecular structure of the N,N,N′,N′,-tetramethylethylenediamine (TMEDA) adduct of dimethylindium iodide was determined. This structure and the available data on the other complexes are discussed here.

Preparation of the Complexes

The ligands used in this work are shown in Table 2.

Table 2 Ligands reacted with dimethylindium iodide.

Ligand	Abbreviation	Formula
N,N,N′,N′-tetramethyl ethylenediamine	TMEDA	$(Me_2N)_2(CH_2)_2$
Triphenylphosphine	-	Ph_3P
1,1-bis(diphenylphosphino) methane	DPPM	$(Ph_2P)_2CH_2$
1,2-bis(diphenylphosphino) ethane	Diphos	$(Ph_2P)_2(CH_2)_2$
Triphenylarsine	-	Ph_3As

All samples of dimethylindium iodide were prepared as outlined above.

The 1:1 adducts of dimethylindium iodide with all ligands other than TMEDA were prepared by slowly mixing toluene solutions of the two reactants using 1:1 molar ratios. TMEDA was added as the neat liquid and $Me_2InI.TMEDA$ is the only complex that precipitates readily. In all other cases the solvent was removed under vacuum. Although the 1:1 adduct with triphenyl phosphine has been reported, very few details were given and it has therefore been studied here for comparative purposes. All the adducts are colourless - white solids. The phosphine and, especially, arsine-based complexes appear to be rather unstable. Clark and Pickard reported that $Me_2InI.PPh_3$ has a substantially lower than expected molecular weight in benzene, suggesting that it

is significantly dissociated.[112] N.M.R. spectra and mass spectra suggest that the same situation occurs for the related complexes reported here. The triphenylarsine complex would be expected to be fragile, but the instability of the phosphine complexes is interesting in view of the fact that trimethylindium forms stable complexes with polydentate phosphines[153] which can be crystallised at ambient temperature and pressure. The organoindium halides would be expected to be stronger Lewis acids. The trialkyl complexes all have a 1:1 indium:phosphorus ratio and it is quite probable therefore that similar organoindium halide species would also be stable. Another factor complicating the chemistry of organoindium halides with weak donors is the dimeric structure of the organoindium halides which must be disrupted by any ligand.

Spectroscopic Properties

Nuclear Magnetic Resonance Spectra

The ^{1}H and ^{31}P N.M.R. data for the complexes are reported in Tables 3 and 4 respectively. Results from more than one spectrum are included for some complexes.

These results clearly show that a significant interaction occurs in solution between dimethylindium iodide with all of the ligands except triphenylarsine. In the ^{1}H spectra the In-CH_3 resonances are typically shifted about 0.5 ppm upfield from about 0.80 ppm for free Me_2InI to around 0.30 ppm in most of the adducts. Conversely, the methylene protons in DPPM, diphos and TMEDA are moved approximately 0.3 ppm downfield on complexation. The variable integrals, however, suggest that the complexes are weak. Washing with hydrocarbon solvents removes ligand, and the excess ligand apparently present in some samples may also be due to their greater solubility than dimethylindium iodide. The chemical shifts in the ^{1}H N.M.R. spectrum of $Me_2InI.AsPh_3$ are essentially identical to those of the starting materials so this complex is probably very weak.

Attempts to obtain useful ^{75}As spectra of $AsPh_3$ and $Me_2InI.AsPh_3$ were unsuccessful.

Table 3. ^1H N.M.R. Data for the dimethylindium iodide adducts and parent ligands in $CDCl_3$

Compound	δ/p.p.m. (multiplicity*, integral)
TMEDA	2.40 (s, 4) 2.25 (s, 12)
$Me_2InI.TMEDA$	2.63 (s, 4) 2.53 (s, 12) 0.30 (s, 6)
PPh_3	7.39 (m)
$Me_2InI.PPh_3$	7.5 (m, 15) 0.30 (s, 5.1)
	7.5 (m, 15) 0.30 (s, 4.90)
DPPM	7.50, 7.36 (2 x m, 20) 2.83 (s, 2)
$Me_2InI.$ DPPM	7.6-7.2 (m, 20) 3.20 (tr, 2) 0.28 (s,6)
	7.55-7.25 (m, 20) 3.08 (tr, 2) 0.28 (s, 6)
	7.55-7.25 (m, 20) 3.08 (tr, 2) 0.80 (s,1.1) 0.18(s, 3)
	7.55-7.25 (m, 20) 2.95 (s, 0.5) 0.15 (s,2.5)
Diphos	7.37 (s, 20) 2.08 (tr, 4)
$Me_2InI.$ diphos	7.45 (s, 20) 2.37 (s, 4) 0.20 (s, 6)
$AsPh_3$	7.38 (s)
$Me_2InI.AsPh_3$	7.39 (s, 15) 0.77 (s, 4.3)
	7.40 (s, 15) 0.77 (s, 4.09)
	7.7 (m, 3) 0.78 (s, 6)

* **Note** s = singlet, tr = triplet, m = multiplet.

Table 4 ^{31}P N.M.R. data for the dimethylindium iodide adducts and parent ligands in C_7H_8/C_7D_8

Ligand	^{31}P Chemical Shift, p.p.m. relative to PPh_3	
	Uncomplexed	Me_2InI adduct
PPh_3	0	-6.12
$2PPh_3$	0	-18.46
DPPM	-16.61	-17.02
Diphos	-6.58	-9.14

Note - Chemical shift of PPh_3 = -5.43 p.p.m. rel. to H_3PO_4

^{31}P N.M.R. spectra also indicate that phosphine complexes are present in solution. In all cases the ^{31}P resonance of the adduct is shifted upfield from that of the free ligand. Addition of approximately one equivalent of triphenylphosphine to $Me_2InI.PPh_3$ moves the resonance even higher upfield. Only one peak was observed, even down to -46°C, showing that ligand interchange is very facile. This also suggests that small quantities of phosphine impurities will significantly alter the observed chemical shifts - the ^{31}P chemical shift of $Me_2InI.PPh_3$ has previously been reported as 11.4 ppm in $CDCl_3$.[70]

It was observed on several occasions that a white precipitate would appear in samples that were left standing for several hours. This may also be relevant to the difficulty found in obtaining ^1H N.M.R. spectra with satisfactory integrals. While reaction with a solvent such as $CDCl_3$ is a possible explanation, it is perhaps more likely that a disproportionation reaction had occurred to produce an insoluble product. The adduct of methylindium dichloride with 2,2'-bipyridine is known to precipitate from solutions containing dimethylindium chloride and bipyridine,[158] the postulated reaction being:-

$$2Me_2InCl(bipy) \rightleftharpoons MeInCl_2(bipy)\downarrow + Me_3In(bipy)$$

Methylindium diiodide could precipitate from dimethylindium iodide solutions because it has an ionic structure in the solid state, $[Me_2In]^+[InI_4]^-$.[13]

Mass Spectra

Mass spectra again provide valuable evidence that the intended complexes are formed, particularly $Me_2InI.AsPh_3$. The C.I. mass spectrum of $Me_2InI.PPh_3$ has already been reported.[70] An $(M + 2)^+$ ion, m/z 536 was observed. No molecular ion was recorded in the E.I. spectra of the DPPM or "diphos" adducts, but small peaks at $(M-15)^+$, corresponding to the loss of a single methyl group, were present. Significantly, a molecular ion was prominent

in the E.I. spectrum of $Me_2InI.AsPh_3$ and one higher mass peak was also recorded. The spectrum of $Me_2InI.TMEDA$ contains no molecular ion but an $(M-2)^+$ peak was found at m/z 386. The major indium-containing peaks of the E.I. spectra are summarised in Tables 5 - 9.

Table 5. Major indium-containing fragments from $Me_2InI.TMEDA$

m/z	Rel.Int. (%)	Assignment
386	12.5	$(M-2)^+$
272	6.8	$(Me_2InI)^+$
261	35.6	$(Me_2In.TMEDA)^+$
257	56.8	$(MeInI)^+$
231	23.9	$(In.TMEDA)^+$
145	88.1	$(Me_2In)^+$
130	16.6	$(MeIn)^+$
115	100.0	In^+

Table 6 Major indium containing fragments from $Me_2InI.PPh_3$

m/z	Rel.Int (%)	Assignment
519	10.1	$(MeInI.PPh_3)^+$
407	18.6	$(Me_2In.PPh_3)^+$
377	15.6	$(In.PPh_3)^+$
272	3.5	$(Me_2InI)^+$
145	66.6	$(Me_2In)^+$
115	50.6	In^+

Table 7 Major indium containing fragments from $Me_2InI.DPPM$

m/z	Rel.Int.(%)	Assignment
641	1.4	$(MeInI.DPPM)^+$
529	3.8	$(Me_2In.DPPM)^+$
499	3.3	$(In.DPPM)^+$
145	11.4	$(Me_2In)^+$
115	12.8	In^+

Table 8 Major indium containing fragments from Me_2InI. diphos.

m/z	Rel. Int.(%)	Assignment
655	2.1	$(MeInI.\ diphos)^+$
543	3.8	$(Me_2In.\ diphos)^+$
513	4.6	$(In\ diphos)^+$
145	11.4	$(Me_2In)^+$
115	12.9	In^+

Table 9 Major indium containing fragments from $Me_2InI.AsPh_3$

m/z	Rel.Int(%)	Assignment
578	54.9	M^+
145	61.4	$(Me_2InI)^+$
130	9.2	$(MeIn)^+$
115	77.6	In^+

Molecular ions from the ligand occur in all of the spectra and high mass peaks due to fragments and rearrangement products are prominent in those of the phosphine and arsine adducts. m/z 262 $(PPh_3)^+$ and m/z 183 $(PPh_2\text{-}2H)^+$

are present in all three phosphine spectra. Important triphenylphosphine fragments are m/z 108 $(PhP)^+$ and m/z 445 $(262 + 183)^+$. Peaks derived from DPPM include m/z 307 $(L\text{-}Ph)^+$, m/z 199, $(Ph_2PCH_2)^+$, 121, $(C_6H_4PCH_2)^+$ and m/s 583, $(383 + 199)^+$. Diphos can eliminate ethene much more readily than can DPPM, so there is a large peak due to $(Ph_4P_2)^+$ at m/z 370, but m/z 199 and m/z 121 are much less abundant. There is again an $(L\text{-}Ph)^+$ ion, m/z 321. Other significant peaks are m/z 289 (L-HPPh), m/z 275 $(Ph_3PCH)^+$, m/z 185 $(Ph_2P)^+$, m/z 107 $(C_6H_4P)^+$ and again, m/z 583 probably $(398 + 185)^+$–in this case.

Unsurprisingly, triphenylarsine fragmentation is similar to that of triphenylphosphine, m/z 227, $(Ph_2As\text{-}2H)^+$, m/z 152 $(PhAs)^+$, m/z 485, $(Ph_4As_2\text{-}H)^+$ and m/z 534 (306 + 228) are major peaks.

Infra-Red Spectra

I.R. spectroscopy has again been little used due to the problems of detailed interpretation, but a full set of spectra have been obtained for both the ligands and the dimethylindium iodide complexes. The differences between the spectra of the ligands and their complexes are indicated in Table 10. A more detailed listing of the spectra of the complexes is given in the Experimental Section.

Table 10. The differences between the I.R. spectra of the dimethylindium iodide adducts and free ligands.

Ligand, L	Compound	Spectral differences
PPh_3	L	1090(m), 512(m-s), 500(m-s), 493(m-s) 420(w)
	$Me_2InI.L$	1098(m-s), 725(m-s), 710(m-s), 518(m-s), 497(m-s) m-s), 478(w)
$(Ph_2P)_2CH_2$	L	1091(w), 510(w-m)
	$Me_2InI.L$	1485(m), 1356(w), 1103(w-m), 762(w-m), 736(s), 525(w-m), 515(w-m), 485(w-m)
$(Ph_2P)_2(CH_2)_2$	L	-
	$Me_2InI.L$	515(m)
$AsPh_3$	L	-
	$Me_2InI.L$	-
TMEDA	L	2970(s), 2940(s), 2860(s), 2808(s), 2762(s), 1465(s), 1270(m), 1160(m), 1140(m), 835(w)
	$Me_2InI.L$	1343(s), 1248(w), 1222(w), 1210(m), 1180(m), 1165(w), 1155(w), 1081(s), 1068(m), 1058(m), 1003(s), 847(s), 820(w), 785(s), 640(w), 582(m), 532(m), 505(w), 486(w)

The spectra of the triphenylphosphine and DPPM adducts show a number of small differences in comparison with the free ligands, but no detailed interpretation can be advanced here.

The spectra of ligand and complex differs only by the presence of a band at 515 cm^{-1} for the diphos adduct, and the spectra of $AsPh_3$ and $Me_2InI.AsPh_3$

are essentially identical. This casts doubt on the composition of the samples of the complexes used to obtain the spectra, and is consistent with the problems in isolating and purifying these compounds noted earlier.

The details of the spectra of TMEDA and Me_2InI.TMEDA are almost totally different. In this case, however, it is difficult to make meaningful comparions of the spectra because TMEDA is a liquid at room temperature, and therefore its spectrum was obtained of a liquid film, while the adduct is a solid and the spectrum was therefore run as a Nujol mull, as for all the other compounds discussed here.

X-Ray Crystallographic Results

It was noted in the introduction to this chapter that one of the main aims of this work was to determine the crystal structure of at least one organoindium halide-phosphine adduct. Unfortunately, this was not achieved, but the crystal structure of the dimethylindium iodide-TMEDA complex was determined, in order to provide information on the nature of the adduct in the solid state. This is valuable because not only could the adduct exist as a molecular unit, monomeric or polymeric, but it could conceivably have an ionic structure, for example $[Me_2In(TMEDA)]^+I^-$. The results of the X-ray study are discussed in this section, and confirm that the structure is molecular in this case. Views of the structure are shown in Figures 1 and 2. The structure is similar to that of the ethylindium diiodide-TMEDA adduct.[229] In both cases the indium atom is in a distorted trigonal-bipyramidal environment. Both structures are shown together in Figure 3. The bond lengths and bond angles of the two compounds are compared in Tables 11 and 12, respectively. It can be seen that the differences between these parameters in the two structures are mostly very small.

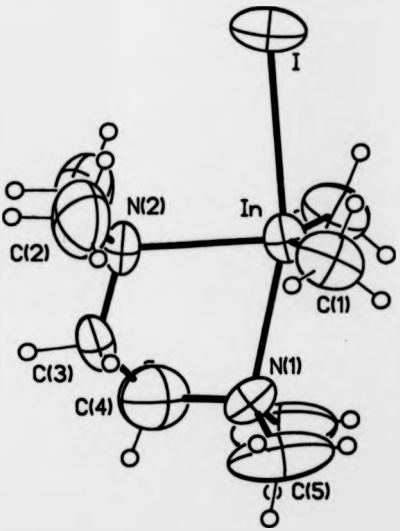


Figure 1 The molecular structure of $Me_2InI.TMEDA$

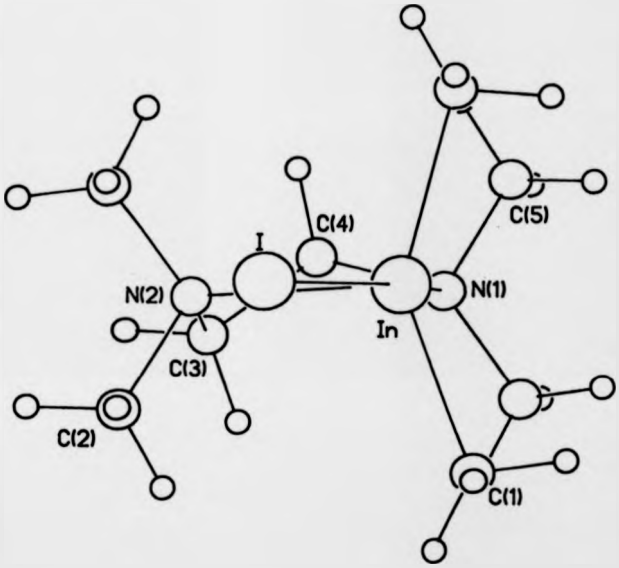


Figure 2 Another view of the structure of $Me_2InI.TMEDA$, looking almost directly down the In-N(1) bond to show the buckled chelate ring.

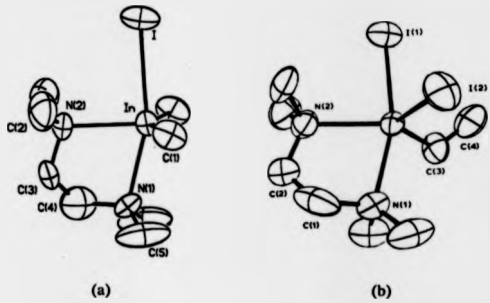


Figure 3. The molecular structures of (a) $Me_2InI.TMEDA$ and (b) $EtInI_2.TMEDA$

Table 11 Bond lengths (Å) in $Me_2InI.TMEDA$ and $EtInI_2.TMEDA$

$Me_2InI.TMEDA$		$EtInI_2.TMEDA$[229]	
In - I	3.183 (4)	In - I (1)	2.919 (1)
		In - I (2)	2.750 (1)
In - C (1)	2.119 (10)	In - C (3)	2.17 (1)
In - C (2)	2.119 (10)		
In - N (1)	2.527 (11)	In - N (1)	2.44 (1)
In - N (2)	2.328 (11)	In - N (2)	2.33 (1)
		C (3) - C (4)	1.42 (2)
N (1) - C (4)	1.451 (26)	N (1) - C (1)	1.50 (2)
N (2) - C (3)	1.489 (25)	N (2) - C (2)	1.44 (2)
C (3) - C (4)	1.490 (37)	C (1) - C (2)	1.46 (2)

Table 12 Bond angles (°) in $Me_2InI.TMEDA$ and $EtInI_2.TMEDA$

Position	$Me_2InI.TMEDA$		$EtInI_2.TMEDA$[229]	
ax-ax	I-In-N(1)	164.4(2)	I(1)-In-N(1)	163.9(3)
ax - eq	I-In-N(2)	89.8(3)	I(1)-In-N(2)	88.7(3)
	I-In-C(1)	90.5(3)	I(1)-In-I(2)	93.3(0)
	I-In-C(1a)	90.5(3)	I(1)-In-C(3)	98.6(5)
	N(1)-In-N(2)	74.6(4)	N(1)-In-N(2)	75.2(4)
	N(1)-In-C(1)	94.4(3)	N(1)-InI(2)	92.3(2)
	N(1)-In-C(1a)	94.4(3)	N(1)-In-C(3)	92.2(5)
eq-eq	N(2)-In-C(1)	108.8(4)	N(2)-In-1(2)	106.9(3)
	N(2)-In-C(1a)	108.8(4)	N(2)-In-C(3)	134.1(5)
	C(1)-In-C(In)	142.4(7)	C(3)-In-I(2)	117.7(4)
–			In-C(3)-C(4)	115.(1)
C.R.	In-N(1)-C(4)	102.6(12)	In-N(1)-C(1)	101.7(8)
	In-N(2)-C(3)	108.6(9)	In-N(2)-C(2)	112.5(9)
	N(1)-C(4)-C(3)	110.4(19)	N(1)-C(1)-C(2)	114(1)
	N(2)-C(3)-C(4)	109.8(22)	N(2)-C(2)-C(1)	111(1)

ax = axial, eq = equatorial, C.R. = chelate ring.

In the dimethylindium iodide adduct the indium-carbon bonds are shorter and the axial indium-nitrogen bond longer than in the ethylindium diiodide, but within known ranges.[2a] At 3.18Å, the In-I bond is nearly 0.2Å longer than the longest (axial) bond in $EtInI_2.TMEDA$, which is in turn about 0.15Å longer than the equatorial In-I distance. The mean distance in the four-coordinate anion, $[EtInI_3]^-$ are even shorter, 2.718(1)Å.[229] These values represent our total knowledge of organoindium-iodine bond lengths so while it can be claimed that $Me_2InI.TMEDA$ contains the longest organoindium-iodine distance yet reported, the significance of this is difficult to assess. For reference, the mean In-I bond length in In_2I_6 is 2.740Å.[233] The tendency for indium bonds to atoms in axial positions to be longer than those to the same element in equatorial

positions has been noted previously with other trigonal bipyramidal indium compounds.[234]

The only significant differences in the bond angles between these two compounds are the changes in the angles separating atoms in the equatorial plane around indium, caused primarily by the presence of a methyl group instead of an iodine atom. Replacement of an ethyl group with a methyl group will also contribute. The N-In-N bond angle of approximately 74° in both these compounds is very close to the value of 76.0(2)° found in the dimethylindium-oxamidine complex, where a four-coordinate indium atom is part of a five-membered chelate ring.[171]

CHAPTER 5

An Examination of Three New Potential Methods for the Production of Gallium and Indium Trialkyls

CHAPTER 5 An Examination of Three New Potential Methods for the Production of Gallium and Indium Trialkyls

Introduction

The work described in this chapter was carried out during a month-long industrial placement at the premises of our collaborating body, Octel, at Ellesmere Port. The aim was to investigate the possibility of producing the valuable gallium and indium triakyls using lead tetralkyls produced by the company. Three approaches were used in this study, as outlined below:

(i) The interaction between the metals gallium and indium and the lead tetraalkyls, according to the equation:-

$$3R_4Pb + 4\,M \longrightarrow 4R_3M + 3Pb\downarrow \quad (M = Ga, In)$$

(ii) The reaction between alkyl halides, gallium and sodium in an autoclave.

$$3RX + Ga + 3Na \longrightarrow R_3Ga + 3NaX$$

(iii) Finally, exchange reactions involving gallium and indium trichlorides with lead tetraalkyls were studied.

$$4MX_3 + 3PbR_4 \rightleftharpoons MR_3 + PbX_4$$

The above schemes, together with the results obtained, are now discussed in more detail.

Reaction of Lead Tetralkyls with Gallium and Indium Metals

The analogous reaction involving mercury dialkyls is a standard preparation of Group 13 (and many other) alkyls. This method is potentially very attractive. The starting materials are the cheapest possible and they contain no halogens or oxygen, which is important for application of the products in the

preparation of semi-conductors. The materials are also fairly easily handled in that the lead alkyls are not very air sensitive, although they are toxic and likely to explode if heated to around 100°C. Gallium and indium metals are convenient to use, bearing in mind the low melting point of gallium.

In this work a number of variations in the reaction conditions were tried as follows:

(a) Gallium with excess of 20% (v/v) solutions of tetraethyllead in toluene and tetrahydrofuran. After stirring at room temperature for 24 hours, the temperature was raised to 40°C (for toluene) and 30°C (for tetrahydrofuran) for 1 hour. The mixture was then subjected to ultrasound treatment for a further 24 hours. Approximately 1/10 of an equivalent of aluminium foil was then added in an attempt to stimulate the reaction (see below), the ultrasound was again applied briefly, and the mixture left stirring overnight.

(b) Gallium was mixed with a two-fold excess of pure tetraethyllead and the ultrasound applied for 4 hours. Indium was also used and in this case the mixture was irradiated with ultrasound for 48 hours.

(c) The reaction between indium and excess Et_4Pb was repeated in the presence of 1/10 an equivalent (with respect to indium metal) of indium(III) chloride. It was considered possible that the more polar organolead halides which should be produced would be more likely to react with indium metal.

Unfortunately no triethylgallium or - indium was detected by gas chromatography - mass spectrometry (g.c.m.s.) in any of the samples taken at each stage of the experiments described above. This was disappointing because it has been reported that small quantities of pure trimethyl- and triethylgallium

were produced by the reactions between Me_4Pb and Et_4Pb with gallium in a distillation column.[235]

Time did not permit attempting a high temperature reaction - to be performed safely on a useful scale would require carefully designed apparatus.

The unreactivity of aluminium in (a) was unexpected because, reputedly, it can undergo a violent reaction with lead tetraalkyls, presumably forming metallic lead and aluminium trialkyls. The use of aluminium is forbidden in the Octel production facilities.

The Reaction between Gallium, Sodium, and Ethyl Halides.

Attempts to react ethyl chloride and ethyl bromide with gallium-sodium alloy were also unsuccessful. Ethyl bromide and toluene were added to some gallium-sodium alloy. (1:3 Ga:Na mole ratio, approximately 50% Ga by weight). After being left stirring for 3 days, no triethylgallium could be detected by g.c.m.s. The mixture was then heated to 40°C for several hours but again no reaction was observed.

The reaction between ethyl chloride and the same alloy in an autoclave at 50°C also failed to produce any detectable quantity of triethyl-gallium.

It is possible that the sodium content of the alloy used was too high as this is known to reduce yields in the production of lead tetraalkyls from lead-sodium alloy and alkyl halides.[2e]

Exchange Reactions between Gallium(III) and Indium(III) Chlorides and Tetramethyl- and Tetraethyllead.

This was the final group of reactions investigated. In the reactions reported here a halide:alkyl mole ratio of approximately 4:3 was used, to test the hypothetical equation below. It was appreciated that an alternative pathway could also produce the mixed alkyl metal halide derivatives of both Ga (or In) and lead and that $PbCl_4$ is rather unstable.

$$4MCl_3 + 3PbR_4 \rightarrow 4MR_3 + 3PbCl_4 \qquad (1)$$

(M = Ga,In; R = Me, Et)

The reactions were again carried out at room temperature using a small quantity (10 cm^3) of n-hexane as solvent. Very slightly more than the required amount of lead alkyl was used. In all cases the reaction mixture was left stirring for at least 24 hours. Small (≈ 1 cm^3) samples of the solution were taken for analysis. The solvent was then pumped off under vacuum yielding slightly sticky white solids. These were heated to about 100°C under vacuum for approximately 1 hour, after which the methyl derivatives were completely solid, while the ethyl compounds were still slightly sticky.

G.c.m.s. analyses again showed that no MR_3 was formed, but the leadtetraalkyls were effectively removed from the solvent, suggesting that partial exchange reactions occurred to produce mixtures of lead and gallium (or indium) organometallic halides. This result is not unexpected. The identity of the products has not been established conclusively, but the evidence given below suggests that the main products are probably trialkyllead chlorides and the dialkylmetal chlorides of gallium (and indium). Attempts to reduce these mixtures with sodium or lithium in refluxing n-hexane were not very successful. Some grey precipitate was observed but yet again no R_3M species were found. This is somewhat surprising.

Unfortunately due to lack of time the reaction

$$MCl_3 + 3PbR_4 \rightarrow MR_3 + R_3PbCl \qquad (2)$$

(M = Ga, In; R = Me, Et)

was not attempted.

This reaction is more likely to be successful. Tetramethyllead has been shown to convert boron trichloride to trimethylborane[236], but on mixing with dimethylaluminium chloride only methyl exchange occurs.[237]

$$Me_3PbMe^* + Me_2AlCl \rightarrow Me_4Pb + Me^*AlMeCl$$

The tentative identification of the organometallic halides produced in reaction (1) is based on the combination of evidence from the mass spectra, and N.M.R. and I.R. spectra. An attempt to separate the products of the reaction between $GaCl_3$ and $PbMe_4$ by sublimation was unsuccessful.

The E.I. mass spectra of the methyl derivatives are informative. The lead isotope ratio, typically, ^{204}Pb (1.5%), ^{206}Pb (23.6%), ^{207}Pb (22.6%), ^{208}Pb (52.3%)[1] aids identification of lead based fragments, and the ions Me_2PbCl^+ (m/z 273 for ^{208}Pb) and Me_3Pb^+ are very prominent in these spectra. This is consistent with the presence of trimethyllead chloride in the product, but not conclusive proof. No molecular ions are observed, but such behaviour is typical of organolead compounds.[2e] Also, even if ions such as $[Me_3PbCl]^+$ had been detected these would have to be regarded with caution, because of the known tendency of organolead halides to disproportionate on heating.[2e]

$$2R_3PbX \rightleftharpoons R_4Pb + R_2PbX_2$$

$$2R_2PbX_2 \rightleftharpoons R_3PbX + RPbX_3$$

$$RPbX_3 \rightarrow RX + PbX_2$$

The products obtained in this work have been heated twice, once when "drying", and again in the spectrometer source.

More useful and reliable evidence is obtained from the abundance of ions Me_2M^+ and $MeMCl^+$ (M = Ga, In) which clearly demonstrates that alkyl-halogen exchange has occurred.

The spectra of the ethyl derivatives are less useful. The ethyl-gallium mixture shows the expected organo-lead peaks, albeit low abundance, but no ethyl gallium peaks are observed. In^+ (m/z 115) is present in the spectrum of the ethyl-indium mixture, but no other ions of significance. The N.M.R. spectra provide similar evidence. The ^1H and ^{13}C spectra, recorded in C_6D_6, are summarised below. A major hinderance to certain interpretation is the unexpected sparsity of literature values with which to compare these results.

Table 1. ^{1}H N.M.R. Spectra of the Organometallic Chloride Mixtures.

Reactants	Major Peaks (ppm)	Multiplicity	Relative Integral		$^{2}J(^{207}Pb..^{1}H)$ (Hz)	Assignment
Me_4Pb, $GaCl_3$	0.45	s	~ 0.2	1.0		? Me_2GaCl
	0.62	s	~ 0.8			
	1.90*	s		2.4	67.2	? Me_3PbCl
	2.07	s				
	2.24*	s				
Me_4Pb, $InCl_3$	0.53	s	~ 0.8	1.0		
	0.60	s	~ 0.2			
	1.90*	s		3.2	68.7	? Me_3PbCl
	2.07	s				
	2.24*	s				
Et_4Pb, $GaCl_3$	1.08	q	1.0			
	1.48	tr	2.3			
	2.17	tr	1.3			? Et_3PbCl
	2.59	q	1.4			
Et_4Pb, $InCl_3$	1.47	m	1.0			
	1.80	s + m	0.3			
	2.21	m	1.6			
	2.65	m	1.6			
	3.13	m	0.4			
	3.36	m	0.6			

* ^{207}Pb satellite peaks

Table 2 ^{13}C N.M.R. Spectra of the Organometallic Chloride Mixtures

Reactants	Major Peaks (ppm)	$J(^{207}Pb...^{13}C)$ (Hz)	Assignment
Me_4Pb, $GaCl_3$	2.31		? Me_2GaCl
	22.94*		
	25.03	210.9	? Me_3PbCl
	27.13*		
Me_4Pb, $InCl_3$	22.17*		
	24.46	230.4	? Me_3PbCl
	26.75*		
Et_4Pb, $GaCl_3$	9.91		
	10.14		
	11.84		
	13.33*		
	13.74	41.7	? Et_3PbCl
	14.16*		
	36.53*		
	37.95	142.7	? Et_3PbCl
	39.37*		
	74.21		
Et_4Pb, $InCl_3$	11.83		
	13.36*		
	13.78	42.3	? Et_3PbCl
	14.20*		
	35.99*		
	37.49	152.0	? Et_3PbCl
	39.01*		
	60.01		
	71.42		

* lead satellite peaks

The peaks due to organolead compounds are easily recognised, except in the ^{1}H spectra of the ethyl derivatives, because of the twin satellite peaks due to coupling with the ^{207}Pb isotope (abundance 22.6%, I = ½). The magnitude of the coupling constants can also be of diagnostic use, although they may vary with concentration.[238] Some literature values for spectral data of the trimethyl and triethyllead chlorides are shown in Table 3.

Table 3. Summary of ^{1}H and ^{13}C N.M.R. spectra of Me_3PbCl and Et_3PbCl

Compound	Solvent	Nucleus	Chemical Shift, p.p.m. (Coupling Constant, Hz)	Ref
Me_3PbCl	$CDCl_3$	^{1}H	1.60(= 70)	238
	$CDCl_3$	^{13}C	21.3(318)	239
Et_3PbCl	$CDCl_3$	^{13}C	$^{13}CH_2$, 35.0(205) $^{13}CH_3$, 12.9 (43)	239
	C_6H_6	^{13}C	$^{13}CH_2$, 36.2 (228)	239

It can be seen that the relevant values in Tables 1 and 2 are similar to those in Table 3, suggesting that the trialkyllead chlorides are present. The chemical shifts are not identical, the discrepancies being greatest for the ^{1}H spectra. This can probably be accounted for in part by solvent and concentration effects, but some degree of complex formation between the products is also likely, for example, related aluminium compounds, $PbCl_2{\cdot}2MeAlCl_2$, $Me_2PbCl_2{\cdot}2MeAlCl_2$ and $Me_3PbCl{\cdot}MeAlCl_2$ have been reported.[237,240,241] Complexation appears to move the ^{1}H resonances of both components downfield.[241] The ^{1}H spectrum of Me_2PbCl_2 has been recorded in DMSO and the ^{2}J ($^{207}Pb{\cdots}^{1}H$) coupling constant was found to be 154.5 Hz.[242] Low solubility has prevented spectra being obtained in non-coordinating solvents, but other dimethyllead derivatives, such as $Me_2Pb(acac)_2$ have very similar coupling

constants in $CHCl_3$.[243] This low solubility implies that the presence of significant amounts of dialkyllead chlorides in our N.M.R. samples is unlikely and raises the important point that unless a solid is completely soluble, an N.M.R. spectrum may not be representative of the sample as a whole.

The precise identity of the gallium and indium products is less clear. Reported ^1H N.M.R. results for the Me_2GaCl, $MeGaCl_2$ and $EtGaCl_2$ in CCl_4 are 0.27, 0.80 and 1.32 and 1.38 p.p.m. respectively.[129] These do not correspond closely to any of the values in Table 1. If complexation does always result in a downfield displacement of the methylmetal resonances, this suggests that significant proportions of Me_2GaCl are present in the mixtures. Indium probably behaves in an analogous manner. The identity of the ethylgallium and, especially, the ethylindium products cannot be proven with certainty on the basis of the N.M.R. evidence described here. It is likely that the products formed are analogous to those in the tetramethyllead reactions. Again, it can only be assumed that indium forms products equivalent to those of gallium.

The use of infra-red spectroscopy, while suffering from the usual problems with interpretation, due to complexity, does have the advantage in this case that there is a reasonable amount of relevant literature. Also, because our spectra were run on Nujol mulls solubility is not required and the spectra are therefore representative of the entire sample. As usual, the spectra of the methyl derivatives are easier to interpret.

For both gallium and indium containing products, two pairs of very sharp peaks, one around 490 cm^{-1} (Pb-C_3 assymmetric stretches), the other close to 1145 cm^{-1}, and also a broad, strong $Pb(CH_3)_3$ deformation band around 784 cm^{-1} strongly suggest that trimethyllead chloride is present.[244] Strong absorbances at 837 and 1184 cm^{-1} due to Me_2PbCl_2 were not noted. The spectrum of Et_3PbCl is altogether less distinctive although strong peaks occur at 680 and 1149 cm^{-1}.[245] These are observed, but are not prominent in the spectra of our products.

Surprisingly, the infra-red spectrum of diethyllead dichloride does not appear to have been reported.

Although I.R. spectra for all eight of the possible gallium and indium organometallic chlorides except ethylindium dichloride have been reported[112,121,129,158,193,246,247] it was again not considered possible to make certain identification of our products on the basis of I.R. evidence. Peaks tentatively attributable to both alkylmetal dichlorides and dialkylmetal chlorides are present, but most are slightly shifted from their expected positions, most probably due to complexation. Some completely unidentified bands are also present. These are listed below:-

Table 4. Unassigned bands (cm^{-1}) in the I.R. spectra of the products of the reactions between PbR_4 (R = Me, Et) and gallium(III)chloride and indium(III)chloride.

Reactants			
$Me_4Pb/GaCl_3$	$Et_4Pb/GaCl_3$	$Me_4Pb/InCl_3$	$Et_4Pb/InCl_3$
1590(s)	875(m)	235(s)	1560(m, br)
1385(s)	460(m, br)		1095(m)
600(s)			890(m)
			725(w)

APPENDIX A

The Use of Quantitative N.M.R. Experiments to Investigate the Hydrolysis of Two Organoindium Iodides

APPENDIX A. The Use of Quantitative N.M.R. Experiments to Investigate the Hydrolysis of Two Organoindium Iodides

This appendix describes a short series of experiments carried out to discover the number of methylindium groups that survive hydrolysis of Me_2InI and $Me_3In_2I_3$. The basis of the method is the comparison of the integrals from ^1H N.M.R. spectra of a known mass of organometallic halide and a known mass of a standard, using the equations below.

$$n_1 = \frac{n_2 I_1 m_2 M_1}{I_2 m_1 M_2} \qquad (1)$$

where n_1 = unknown number of protons in the peak, per mole of compound 1 (in this case Me_2InI or $Me_3In_2I_3$)

I_1 = integral for that peak

m_1 = mass of sample of compound 1

M_1 = molecular weight of compound 1

n_2, I_2, m_2 and M_2 are the equivalent parameters for a standard compound. 1,3,5-Trioxane $(-CH_2O-)_3$, was chosen as a standard for several reasons. It is an unreactive solid, easily weighed, and its ^1H N.M.R. spectrum contains only one resonance, a singlet. It also has a reasonably small number of protons per unit mass and the useful (but not essential) property of being soluble in both $CDCl_3$ and D_2O. The only disadvantage is that its resonance, at about 5 ppm, is close to both CH_2Cl_2, which is a useful reference for spectra of organometallic compounds and the residual protons in D_2O. It is therefore advisable to run a spectrum of the D_2O used to measure the HOD integral. Using trioxane, n_2 equals six and M_2 is 90.08, hence equation (1) becomes:-

$$n_1 = \frac{6(I_1 m_2 M_1)}{90.08(I_2 m_1)} \qquad (2)$$

Table 1 shows the experimental results obtained from a 220 MHz C.W. spectrometer. Integrals were measured to the nearest half-millimetre.

Table 1 The Results of the Quantitative N.M.R. Experiments

Solvent	Indium Compound	Sample Mass (mg)	$InCH_3$ integral (mm)	Mass of Tricosane (mg)	Tricosane Integral (mm)	n_1 from equ 2
$CDCl_3$	Me_2InI (Mol.W. 271.80)	53	33.0	22	40.0	6.2
D_2O	Me_2InI	53	62.0	19	71.0	5.7
D_2O	Me_2InI	44	20.0	21	28.5	6.1
$CDCl_3$	$Me_3In_2I_3$ (Mol.W. 653.46)	44	20.0	10	22.0	9.0
D_2O	$Me_3In_2I_3$	39	31.0	12	52.0	8.0
D_2O	$Me_3In_2I_3$	39	32.5	12	54.0	7.7
D_2O	$Me_3In_2I_3$	57	61.0	9	44.0	9.6

Values of n_1 were obtained for unreacted samples of the organoindium iodides in deuterochloroform to establish the validity of the technique. Ideally, more measurements should have been taken for both $CDCl_3$ and D_2O solutions and use of the 400 MHz F.T. spectrometer would obtain more accurate integrals. The results here, do however, provide good evidence for the hypothesis that for Me_2InI and $Me_3In_2I_3$ all methylindium groups survive hydrolysis. Although not unexpected, this is a useful result because the 220 MHz spectrum of the hydrolysed sesquiiodide appears to contain only one methylindium resonance, in the same position as that in the Me_2InI spectrum, which could lead to the apparently erroneous conclusion that only dimethylindium groups survived. Closer examination revealed that two almost coincidental singlets may be

present. An alternative possibility is that a methyl redistribution reaction has occurred:-

$$2\ MeIn_{aq}^{2+} \longrightarrow Me_2In^{+}_{aq} + In_{aq}^{3+}$$

To investigate this, ^1H and ^{13}C spectra of a solution of $Me_3In_2I_3$ in D_2O (containing no trioxane) were run on the 400 MHz spectrometer. These clearly show that two organoindium species are indeed present in the solution. The results are summarised in Table 2.

Table 2 ^1H and ^{13}C Chemical Shifts of Hydrolysed $Me_3In_2I_3$

	Chemical Shift (p.p.m.)	
Nucleus	$Me_2In_{aq}^{+}$	$MeIn_{aq}^{2+}$
^1H	-0.15	-0.11
^{13}C	-1.66	-4.39

The peaks are assigned on the basis of their relative integrals, those of $Me_2In_{aq}^{+}$ being twice that of $MeIn_{aq}^{2+}$. While ^{13}C integrals must be regarded with some caution, it is noteworthy that they imply that the ^{13}C resonance due to $MeIn_{aq}^{2+}$ occurs upfield from that of $Me_2In_{aq}^{+}$, while the reverse is true for the ^1H shifts.

APPENDIX B

The Preparation of $Br_3In_2(CH_2CO_2Et)_3$

APPENDIX B. The Preparation of $Br_3In_3(CH_2CO_2Et)_3$

In 1975, Chao and Riecke reported the use of activated indium metal and ethyl bromoacetate for Reformatsky reactions.[145] The isolation of $BrIn(CH_2CO_2Et)_2$ was also claimed, based on indium and bromine analyses. We report here the preparation of a material analysing as $Br_3In_2(CH_2CO_2Et)_3$ using indium metal foil.

Indium (0.50g 4.35 mmol) was placed in a Schlenck tube with ethyl bromoacetate (1.08g, 6.47 mmol a slight deficiency).

$$2In + 3BrCH_2CO_2Et \longrightarrow Br_3In_2(CH_2CO_2Et)_3$$

Dry toluene (5 cm^3) and a very small pellet of iodine, to activate the indium, were then added. The solution was degassed and left under vacuum. After ten minutes in an ultrasonic bath the iodine colour disappeared, the indium started to break up and was coated with a dark red substance [probably indium(I)iodide]. The mixture was then left stirring at 60°C, and after 24 h the solution had turned yellow, the indium had broken up, and a fine orange precipitate had appeared. After one week the solution had cleared and was orange in colour. Removal of the solvent under vacuum left a brown-red solid, which was slightly sticky, probably due to traces of unreacted, co-ordinated ethyl bromoacetate. A further small quantity of indium (~ 0.05g) and toluene (5cm^3) were therefore added. The mixture was again degassed and left stirring at 60°C for a further three days. After the solvent was pumped off again a rust-coloured solid (1.45g) remained. A portion (0.60g) of this solid was purified by dissolving the product in dichloromethane (50cm^3), filtering the solution, and removing the solvent. The yield of purified material was 0.36g (55% based on the equation above). Analysis, calculated for $C_{12}H_{21}O_6In_2Br_3$ (M.W. 730.67): C, 19.73; H, 2.90; Br, 32.81%. Found: C, 19.39; H, 2.76; Br, 30.2%. The compound appears to be air stable, it is soluble in dichloromethane and acetonitrile, sparingly soluble in toluene, and insoluble in aliphatic hydrocarbons. Reaction occurs with dimethylsulphoxide, a pale creamy-yellow power precipitating.

Unfortunately, attempts to grow crystals by layering or evaporation methods were unsuccessful, which suggests the compound is polymeric. Further support for this hypothesis comes from the failure of attempts to obtain mass spectra and the poor ^{1}H N.M.R. and I.R. spectra obtained. The ^{1}H N.M.R. spectrum ($CDCl_3$) contains very broad peaks around 1.30 p.p.m. and 4.25 p.p.m. and a sharp singlet at 1.25 p.p.m. The I.R. spectrum is complicated, containing numerous very broad peaks, in particular, a moderately intense band covering the range 310 - 620 cm^{-1}.

APPENDIX C

X-Ray Crystallographic Studies

APPENDIX C. X-Ray Crystallographic Studies

Crystals were grown and mounted by the author. The X-ray crystallographic structure determinations described in this work were carried out by Dr N. W. Alcock and Dr W. Errington.

General Method

All of the crystals used were mounted under argon or nitrogen in thin walled quartz Lindemann tubes (typically of ½ mm diameter) and held in position with a trace of Apiezon grease. They were placed in the Lindemann tubes using a glass fibre and the tubes were sealed, initially with grease and then with wax. For the more air sensitive crystals all of these operations except the application of wax were carried out in a dry nitrogen filled glove box. For the less air sensitive crystals this was done very quickly in air, and the air removed and replaced by nitrogen or argon on a Schlenck line, before sealing.

The diffraction data for all compounds reported here were collected at 290°K, on a Siemens P3R3 four-circle diffractometer in the ω-2θ mode, operating with Mo-Kα graphite monochromatised radiation, λ = 0.71069Å. Three standard reflections were monitored after every 200 reflections and the data were rescaled to correct for any changes in the intensity of these standards that occurred during data collection. Unit cell dimensions were generally obtained by least squares fit to 15 high angle reflections (20 in the case of MeGa ($C_{22}H_{22}N_4$). Reflections with intensities $I/\sigma(I) \geq 2.0$ were considered observed and used in the refinement of the structures. They were corrected for Lorentz, polarisation and absorption effects using the Gaussian method. Structure solution was generally by direct methods (TREF). The structure refinement of each compound is described individually below. H atoms were generally placed in fixed calculated positions with methyl groups refined as rigid bodies. Final refinement was by least squares methods, generally with anisotropic thermal

parameters for all non-H atoms. A weighting scheme of the form $W = 1/(\sigma^2F + gF^2)$ was used and shown to be satisfactory by weight analysis. Computing work was carried out using SHELXTL PLUS on a DEC Microvax II.[248] Scattering factors and anomolous dispersion factors were taken from the literature.[249]

The unit cell data and the data collection parameters for all of the compounds are given together below.

Bond lengths, bond angles, and the atomic co-ordinates of the non-hydrogen atoms of each compound are listed separately in the tables that follow the description of each structure refinement. For unpublished structures (i.e. all except $Me_2GaHtmtaa$), supplementary material comprising of thermal parameters, hydrogen atom co-ordinates and structure factor listings, can be obtained from Dr N.W. Alcock (University of Warwick).

Compound	Dimethylgallium-N,N′-diphenylbenzamidine	N,N′-di(p-tolyl) benzamidine
Formula	$C_{21}H_{21}N_2Ga$	$C_{21}H_{20}N_2$
Mol. Weight	371.1	300.4
Crystal System	Orthorhombic	Orthorhombic
Space group	$P2_1cn$	P2(1)2(1)2(1)
a,(Å)	9.385(4)	11.364(2)
b,(Å)	10.280(10)	16.452(3)
c,(Å)	19.580(15)	18.609(4)
α,(°)	90	90
β,(°)	90	90
γ,(°)	90	90
U,(Å^3)	1889	3479(4)
D_c,(g cm^{-3})	1.30	1.29
Z	4	9
μ(Mo-K_α),(cm^{-1})	14.6	0.8
Total reflections	1785	2166
Total reflections with $I/\sigma(I)\geq 2.0$	1286	1457
Max 2θ,(°)	50	42
2θ Range	± 1.5	± 0.7
Max. and min. transmission factors	0.648, 0.476	-
Crystal size, (mm)	0.53x0.40x0.34	0.28x0.51x0.47
Number of parameters refined	216	307
g	0.0040	0.001043
R	0.047	0.0554
Shift error, final cycle	0.08	0.013

Compound	$Me_2GaHtmtaa$	MeGatmtaa
Formula	$C_{24}H_{29}N_4Ga$	$C_{23}H_{25}N_4Ga$
Mol. Weight	443.2	427.20
Crystal System	Monoclinic	Triclinic
Space group	C2/c	PT
a,(Å)	30.672(13)	9.023(3)
b,(Å)	9.494(4)	11.740(3)
c,(Å)	15.657(5)	11.861(3)
α,(°)	90	107.78(2)
β,(°)	100.24(3)	107.83(2)
γ,(°)	90	107.74(2)
U,($Å^3$)	4486	1023.3(5)
D_c,(g cm^{-3})	1.32	1.39
Z	8	2
μ(Mo-K_α),(cm^{-1})	12.4	0.14
Total reflections	3970	3859
Total reflections with $I/\sigma(I)\geq 2.0$	2465	2684
Max 2θ,(°)	50	50
2θ Range	± 0.6	± 1.3
Max. and min. transmission factors	0.94, 0.78	0.78, 0.86
Crystal size, (mm)	0.044x0.23x0.52	0.14x0.20x0.41
Number of parameters refined	284	268
g	0.0005	0.00537
R	0.054	0.053
R_W	0.054	0.060
Shift error, final cycle	0.2	0.2

Compound	$Me_2InI.TMEDA$
Formula	$C_8H_{22}N_2InI$
Mol. Weight	388.0
Crystal System	Orthorhombic
Space group	Pcmn
a,(Å)	10.148(3)
b,(Å)	10.90(1)
c,(Å)	12.503(5)
α,(°)	90
β,(°)	90
γ,(°)	90
U,(Å^3)	1383.5
D_c(g cm^{-3})	1.62
Z	4
μ(Mo-K_α), (cm^{-1})	39.0
Total reflections	1293
Total reflections with $I/\sigma(I)\geq 2.0$	963
Max 2θ,(°)	50
2θ Range	± 0.75
Max. and min. transmission factors	0.30, 0.67
Crystal size, (mm)	0.10x0.33x0.86
Number of parameters refined	80
g	0.0005
R	0.051
R_W	0.072
Shift error, final cycle	0.04

Dimethylgallium-N,N′-diphenylbenzamidine

The data for this compound showed systematic absences hkO, h + k = 2n + 1; hOl, l = 2n + 1, indicating that the space group was $P2_1cn$ (non-standard setting of $Pna2_1$) or Pmcn (non-standard setting of Pnma). The value of z, combined with statistical tests, suggested $P2_1cn$ which was chosen and shown to be correct by successful refinement. Although in principle the molecule could contain a mirror plane and be placed on the crystallographic plane in Pmcn, the orientation of the phenyl groups do not conform to this symmetry.

Table 1 Bond lengths for Dimethylgallium-N,N′-diphenylbenzamidine (Å)

Ga(1)-N(1)	2.045(7)	Ga(1)-N(2)	2.036(8)
Ga(1)-C(1)	1.944(12)	Ga(1)-C(2)	1.944(11)
N(1)-C(3)	1.331(11)	N(1)-C(11)	1.397(11)
N(2)-C(3)	1.335(11)	N(2)-C(21)	1.384(11)
C(3)-C(31)	1.491(12)	C(11)-C(12)	1.383(12)
C(11)-C(16)	1.386(12)	C(12)-C(13)	1.375(15)
C(13)-C(14)	1.370(16)	C(14)-C(15)	1.359(16)
C(15)-C(16)	1.380(15)	C(21)-C(22)	1.379(13)
C(21)-C(26)	1.403(12)	C(22)-C(23)	1.396(14)
C(23)-C(24)	1.358(16)	C(24)-C(25)	1.395(19)
C(25)-C(26)	1.352(16)	C(31)-C(32)	1.382(12)
C(31)-C(36)	1.384(13)	C(32)-C(33)	1.378(14)
C(33)-C(34)	1.391(17)	C(34)-C(35)	1.354(14)
C(35)-C(36)	1.369(14)		

Table 2 Bond angles for Dimethylgallium-N,N′-diphenylbenzamidine (°)

N(1)-Ga(1)-N(2)	65.0(3)	N(1)-Ga(1)-C(1)	111.0(4)
N(2)-Ga(1)-C(1)	114.1(4)	N(1)-Ga(1)-C(2)	116.8(4)
N(2)-Ga(1)-C(2)	113.3(4)	C(1)-Ga(1)-C(2)	122.8(5)
Ga(1)-N(1)-C(3)	91.9(5)	Ga(1)-N(1)-C(11)	138.5(6)
C(3)-N(1)-C(11)	128.9(7)	Ga(1)-N(2)-C(3)	92.2(5)
Ga(1)-N(2)-C(21)	138.4(6)	C(3)-N(2)-C(21)	128.2(8)
N(1)-C(3)-N(2)	110.8(7)		
N(1)-C(3)-C(31)	124.5(8)	N(2)-C(3)-C(31)	124.6(8)
N(1)-C(11)-C(12)	116.7(8)	N(1)-C(11)-C(16)	123.6(8)
C(12)-C(11)-C(16)	119.5(8)	C(11)-C(12)-C(13)	118.6(8)
C(12)-C(13)-C(14)	122.1(10)	C(13)-C(14)-C(15)	118.9(10)
C(14)-C(15)-C(16)	120.7(10)	C(11)-C(16)-C(15)	120.0(8)
N(2)-C(21)-C(22)	125.6(8)	N(2)-C(21)-C(26)	116.5(8)
C(22)-C(21)-C(26)	117.8(8)	C(21)-C(22)-C(23)	120.6(9)
C(22)-C(23)-C(24)	120.3(10)	C(23)-C(24)-C(25)	119.6(11)
C(24)-C(25)-C(26)	120.1(11)	C(21)-C(26)-C(25)	121.5(10)
C(3)-C(31)-C(32)	120.2(8)	C(3)-C(31)-C(36)	119.3(8)
C(32)-C(31)-C(36)	120.5(8)	C(31)-C(32)-C(33)	119.0(9)
C(32)-C(33)-C(34)	119.8(9)	C(33)-C(34)-C(35)	120.5(9)
C(34)-C(35)-C(36)	120.5(10)	C(31)-C(36)-C(35)	119.7(8)

Table 3 Atomic co-ordinates for Dimethylgallium-N,N′-diphenylbenzamidine

Atom	x	y	z	U
Ga(1)	10864.9	577.5(7)	5613.2(4)	42(1)*
N(1)	10565(8)	1646(7)	4744(3)	41(3)*
N(2)	9521(9)	2120(7)	5715(3)	42(3)*
C(1)	9907(14)	-1095(11)	5550(6)	66(4)*
C(2)	12665(12)	812(10)	6088(6)	65(4)*
C(3)	9660(10)	2443(8)	5058(4)	39(3)*
C(11)	11151(9)	1748(8)	4091(5)	39(3)*
C(12)	11410(11)	596(9)	3748(5)	48(3)*
C(13)	12054(14)	648(10)	3118(6)	64(4)*
C(14)	12500(13)	1795(12)	2834(5)	68(4)*
C(15)	12243(13)	2924(10)	3173(5)	58(4)*
C(16)	11587(12)	2915(8)	3804(5)	47(3)*
C(21)	8555(10)	2598(8)	6187(4)	37(3)*
C(22)	7153(10)	2911(9)	6055(5)	46(3)*
C(23)	6263(11)	3352(10)	6578(6)	64(4)*
C(24)	6771(15)	3484(11)	7224(6)	68(4)*
C(25)	8189(14)	3176(10)	7363(6)	71(5)*
C(26)	9049(12)	2740(9)	6859(5)	52(3)*
C(31)	8863(9)	3513(8)	4716(4)	37(3)*
C(32)	8929(11)	4766(8)	4970(6)	47(3)*
C(33)	8160(13)	5734(8)	4652(6)	56(4)*
C(34)	7354(13)	5443(9)	4075(6)	57(4)*
C(35)	7311(11)	4215(9)	3827(5)	54(3)*
C(36)	8066(11)	3241(9)	4138(5)	44(3)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Atom coordinates ($\times 10^4$) and isotropic thermal parameters ($A^2 \times 10^3$)

N,N′-di(p-tolyl)benzamidine

Systematic absences occurred at hOO, $h \neq 2n$; OkO, $k \neq 2n$; OOl, $l \neq 2n$, indicating that the space group was $P2_12_12_1$.

The structure is shown in Figure 1.

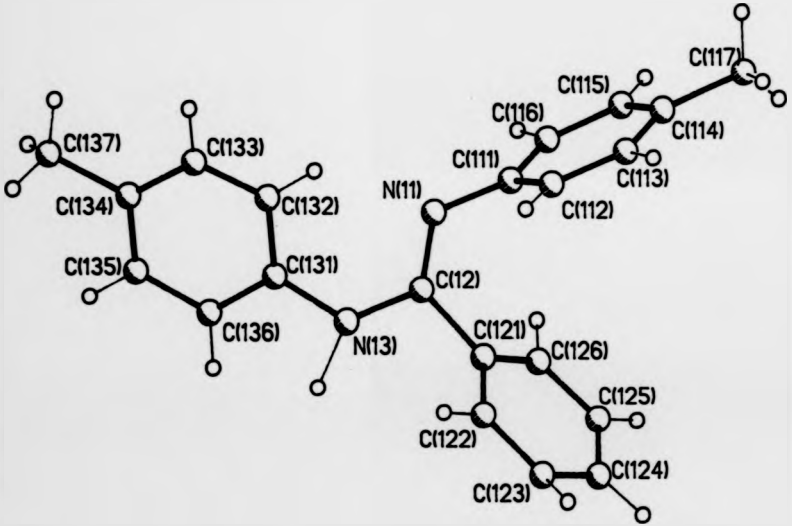


Figure 1 Molecular structure of N,N'- di(p-tolyl)benzamidine

Table 4 Bond lengths for N,N′- di(p-tolyl)benzamidine (Å)

N(11)-C(12)	1.265(12)	N(11)-C(111)	1.396(12)
N(13)-C(12)	1.374(12)	N(13)-C(131)	1.411(12)
N(21)-C(22)	1.313(15)	N(21)-C(211)	1.417(13)
N(23)-C(22)	1.348(13)	N(23)-C(231)	1.427(13)
C(12)-C(121)	1.477(14)	C(111)-C(112)	1.358(15)
C(111)-C(116)	1.349(14)	C(112)-C(113)	1.364(18)
C(113)-C(114)	1.355(17)	C(114)-C(115)	1.351(16)
C(114)-C(117)	1.497(15)	C(115)-C(116)	1.368(14)
C(121)-C(122)	1.385(15)	C(121)-C(126)	1.316(15)
C(122)-C(123)	1.380(17)	C(123)-C(124)	1.372(21)
C(124)-C(125)	1.345(20)	C(125)-C(126)	1.372(17)
C(131)-C(132)	1.380(15)	C(131)-C(136)	1.364(15)
C(132)-C(133)	1.361(16)	C(133)-C(134)	1.330(22)
C(134)-C(135)	1.346(22)	C(134)-C(137)	1.502(15)
C(135)-C(136)	1.409(17)	C(22)-C(221)	1.499(13)
C(211)-C(212)	1.362(15)	C(211)-C(216)	1.339(15)
C(212)-C(213)	1.359(15)	C(213)-C(214)	1.344(16)
C(214)-C(215)	1.372(17)	C(214)-C(217)	1.497(15)
C(215)-C(216)	1.368(15)	C(221)-C(222)	1.349(14)
C(221)-C(226)	1.404(15)	C(222)-C(223)	1.326(17)
C(223)-C(224)	1.342(22)	C(224)-C(225)	1.328(21)
C(225)-C(226)	1.381(18)	C(231)-C(232)	1.381(14)
C(231)-C(236)	1.342(14)	C(232)-C(233)	1.361(18)
C(233)-C(234)	1.344(20)	C(234)-C(235)	1.380(18)
C(234)-C(237)	1.525(17)	C(235)-C(236)	1.361(15)

Table 5 Bond angles for N,N′-di(p-tolyl)benzamidine (°)

C(12)-N(11)-C(111)	120.0(8)	C(12)-N(13)-C(131)	127.3(8)
C(22)-N(21)-C(211)	116.6(8)	C(22)-N(23)-C(231)	128.5(8)
N(11)-C(12)-N(13)	121.2(8)	N(11)-C(12)-C(121)	125.9(9)
N(13)-C(12)-C(121)	112.7(8)	N(11)-C(111)-C(112)	122.1(9)
N(11)-C(111)-C(116)	122.5(9)	C(112)-C(111)-C(116)	115.3(9)
C(111)-C(112)-C(113)	121.9(10)	C(112)-C(113)-C(114)	122.6(11)
C(113)-C(114)-C(115)	119.3(10)	C(113)-C(114)-C(117)	122.1(11)
C(115)-C(114)-C(117)	122.5(10)	C(114)-C(115)-C(116)	122.1(10)
C(111)-C(116)-C(115)	122.6(9)	C(12)-C(121)-C(122)	120.5(9)
C(12)-C(121)-C(126)	120.3(9)	C(122)-C(121)-C(126)	119.2(9)
C(121)-C(122)-C(123)	120.3(10)	C(122)-C(123)-C(124)	118.0(11)
C(123)-C(124)-C(125)	121.3(13)	C(124)-C(125)-C(126)	119.0(12)
C(121)-C(126)-C(125)	122.0(10)	N(13)-C(131)-C(132)	123.6(9)
N(13)-C(131)-C(136)	117.4(9)	C(132)-C(131)-C(136)	119.0(9)
C(131)-C(132)-C(133)	119.0(11)	C(132)-C(133)-C(134)	124.1(13)
C(133)-C(134)-C(135)	116.9(12)	C(133)-C(134)-C(137)	122.6(15)
C(135)-C(134)-C(137)	120.4(15)	C(134)-C(135)-C(136)	122.5(12)
C(131)-C(136)-C(135)	118.3(10)	N(21)-C(22)-N(23)	120.9(9)
N(21)-C(22)-C(221)	125.4(9)	N(23)-C(22)-C(221)	113.6(9)
N(21)-C(211)-C(212)	119.9(9)	N(21)-C(211)-C(216)	120.4(9)
C(212)-C(211)-C(216)	119.5(9)	C(211)-C(212)-C(213)	118.7(9)
C(212)-C(213)-C(214)	124.0(10)	C(213)-C(214)-C(215)	115.7(10)
C(213)-C(214)-C(217)	123.0(10)	C(215)-C(214)-C(217)	121.2(10)
C(214)-C(215)-C(216)	121.7(10)	C(211)-C(216)-C(215)	120.3(10)
C(22)-C(221)-C(222)	122.2(9)	C(22)-C(221)-C(226)	118.4(9)
C(222)-C(221)-C(226)	119.2(9)	C(221)-C(222)-C(223)	121.4(11)
C(222)-C(223)-C(224)	119.8(12)	C(223)-C(224)-C(225)	122.1(13)
C(224)-C(225)-C(226)	119.7(12)	C(221)-C(226)-C(225)	117.8(10)
N(23)-C(231)-C(232)	114.2(9)	N(23)-C(231)-C(236)	125.3(9)
C(232)-C(231)-C(236)	120.3(10)	C(231)-C(232)-C(233)	118.3(10)
C(232)-C(233)-C(234)	122.7(11)	C(233)-C(234)-C(235)	117.7(11)
C(233)-C(234)-C(237)	123.5(12)	C(235)-C(234)-C(237)	118.8(12)
C(234)-C(235)-C(236)	120.9(11)	C(231)-C(236)-C(235)	120.1(10)

Table 6 Atomic co-ordinates for N,N′- di(p-tolyl)benzamidine

Atom	x	y	z	U
N(11)	14195(6)	6588(5)	-1497(4)	56(3)*
N(13)	15156(6)	7284(4)	-2394(4)	50(3)*
N(21)	10005(7)	11548(5)	1349(4)	63(3)*
N(23)	9896(8)	10238(5)	1798(4)	70(3)*
C(12)	14206(9)	7161(6)	-1950(5)	51(4)*
C(111)	13272(8)	6524(6)	-1006(5)	54(4)*
C(112)	13073(11)	7098(6)	-496(6)	95(5)*
C(113)	12184(12)	7026(7)	-7(6)	105(6)*
C(114)	11470(9)	6368(8)	22(6)	74(5)*
C(115)	11677(8)	5792(6)	-481(6)	70(4)*
C(116)	12559(9)	5869(6)	-977(5)	64(4)*
C(117)	10516(9)	6287(7)	572(6)	102(5)*
C(121)	13218(9)	7717(6)	-2107(5)	50(4)*
C(122)	13388(9)	8550(7)	-2109(5)	63(4)*
C(123)	12456(14)	9068(6)	-2238(6)	82(5)*
C(124)	11375(13)	8730(9)	-2378(7)	102(6)*
C(125)	11220(10)	7920(9)	-2381(7)	109(6)*
C(126)	12168(11)	7424(6)	-2255(5)	76(4)*
C(131)	16263(8)	6897(5)	-2359(6)	54(4)*
C(132)	16739(10)	6590(6)	-1733(6)	79(5)*
C(133)	17859(10)	6297(7)	-1743(8)	84(5)*
C(134)	18504(11)	6221(7)	-2335(11)	101(7)*
C(135)	18029(12)	6499(7)	-2950(7)	88(5)*
C(136)	16891(10)	6837(5)	-2981(6)	70(4)*
C(137)	19730(8)	5879(6)	-2328(9)	139(7)*
C(22)	10284(8)	10775(7)	1305(5)	64(4)*
C(211)	10250(9)	12033(6)	737(6)	59(4)*
C(212)	9658(9)	11900(5)	112(6)	62(4)*
C(213)	9861(10)	12403(7)	-454(6)	73(4)*
C(214)	10636(11)	13020(7)	-442(6)	75(5)*
C(215)	11173(11)	13160(6)	206(7)	92(5)*
C(216)	10985(11)	12666(7)	787(5)	80(5)*
C(217)	10857(11)	13559(7)	-1075(5)	112(6)*
C(221)	11082(9)	10408(6)	752(5)	54(4)*
C(222)	10751(10)	9772(6)	341(6)	69(4)*
C(223)	11447(13)	9481(8)	-170(6)	91(6)*
C(224)	12502(15)	9822(10)	-286(6)	102(7)*
C(225)	12882(11)	10452(9)	94(8)	104(6)*
C(226)	12182(11)	10771(6)	631(6)	81(5)*
C(231)	9012(9)	10348(6)	2333(5)	55(4)*
C(232)	8942(11)	9723(6)	2827(5)	75(5)*
C(233)	8053(13)	9738(7)	3317(6)	84(5)*
C(234)	7254(12)	10340(10)	3344(6)	88(6)*
C(235)	7353(10)	10960(7)	2849(6)	79(5)*
C(236)	8227(9)	10957(6)	2348(5)	63(4)*
C(237)	6250(11)	10367(8)	3887(6)	128(6)*

* Equivalent isotropic U defined as one third of the trace of the orthoqonalised U_{ij} tensor

Atom coordinates (x10^4) and isotropic thermal parameters (Å^{2}x10^3)

$Me_2Ga(C_{22}H_{23}N_4)$

Systematic absences occurred at hkl, h + k = 2n; h0l, l = 2n, indicating that the space group is either Cc or C2/c. The latter was selected and shown to be correct by successful refinement. Hydrogen atoms were inserted at calculated positions with that attached to N(1) refined.

Table 7 Bond lengths for $Me_2Ga(C_{22}H_{23}N_4)$ (Å)

Ga-N(2)	1.965(4)	Ga-N(3)	1.985(5)
Ga-C(23)	1.961(6)	Ga-C(24)	1.953(6)
N(1)-C(1)	1.410(8)	N(1)-C(21)	1.343(8)
N(2)-C(6)	1.450(7)	N(2)-C(7)	1.335(8)
N(3)-C(10)	1.320(8)	N(3)-C(12)	1.438(7)
N(4)-C(17)	1.422(7)	N(4)-C(18)	1.314(8)
C(1)-C(2)	1.387(8)	C(1)-C(6)	1.390(8)
C(2)-C(3)	1.376(10)	C(3)-C(4)	1.354(10)
C(4)-C(5)	1.381(9)	C(5)-C(6)	1.380(8)
C(7)-C(8)	1.504(8)	C(7)-C(9)	1.401(8)
C(9)-C(10)	1.399(8)	C(10)-C(11)	1.504(8)
C(12)-C(13)	1.382(8)	C(12)-C(17)	1.388(8)
C(13)-C(14)	1.382(10)	C(14)-C(15)	1.371(10)
C(15)-C(16)	1.383(9)	C(16)-C(17)	1.381(9)
C(18)-C(19)	1.507(9)	C(18)-C(20)	1.407(8)
C(20)-C(21)	1.388(9)	C(21)-C(22)	1.502(8)

Table 8 Bond angles for $Me_2Ga(C_{22}H_{23}N_4)$ (°)

N(2)-Ga-N(3)	90.7(2)	N(2)-Ga-C(23)	107.8(2)
N(3)-Ga-C(23)	110.1(2)	N(2)-Ga-C(24)	108.8(2)
N(3)-Ga-C(24)	110.0(2)	C(23)-Ga-C(24)	124.3(3)
C(1)-N(1)-C(21)	127.8(5)	Ga-N(2)-C(6)	119.1(4)
Ga-N(2)-C(7)	120.6(3)	C(6)-N(2)-C(7)	120.3(4)
Ga-N(3)-C(10)	121.2(4)	Ga-N(3)-C(12)	117.7(4)
C(10)-N(3)-C(12)	120.3(5)	C(17)-N(4)-C(18)	125.7(5)
N(1)-C(1)-C(2)	123.5(6)	N(1)-C(1)-C(6)	118.1(5)
C(2)-C(1)-C(6)	118.3(6)	C(1)-C(2)-C(3)	120.5(6)
C(2)-C(3)-C(4)	120.3(6)	C(3)-C(4)-C(5)	120.8(6)
C(4)-C(5)-C(6)	119.2(6)	N(2)-C(6)-C(1)	117.9(5)
N(2)-C(6)-C(5)	121.0(5)	C(1)-C(6)-C(5)	120.9(5)
N(2)-C(7)-C(8)	120.2(5)	N(2)-C(7)-C(9)	122.4(5)
C(8)-C(7)-C(9)	117.3(5)	C(7)-C(9)-C(10)	125.1(5)
N(3)-C(10)-C(9)	123.1(5)	N(3)-C(10)-C(11)	120.1(5)
C(9)-C(10)-C(11)	116.8(5)	N(3)-C(12)-C(13)	120.1(5)
N(3)-C(12)-C(17)	119.1(5)	C(13)-C(12)-C(17)	120.6(6)
C(12)-C(13)-C(14)	119.8(6)	C(13)-C(14)-C(15)	119.7(6)
C(14)-C(15)-C(16)	120.7(6)	C(15)-C(16)-C(17)	120.0(6)
N(4)-C(17)-C(12)	116.9(5)	N(4)-C(17)-C(16)	123.7(5)
C(12)-C(17)-C(16)	119.1(5)	N(4)-C(18)-C(19)	123.0(6)
N(4)-C(18)-C(20)	120.2(6)	C(19)-C(18)-C(20)	116.6(6)
C(18)-C(20)-C(21)	127.3(6)	N(1)-C(21)-C(20)	119.8(5)
N(1)-C(21)-C(22)	121.8(6)	C(20)-C(21)-C(22)	118.3(6)

Table 9 Atomic co-ordinates for $Me_2Ga(C_{22}H_{23}N_4)$

Atom	x	y	z	U
Ga	1570.8(2)	570.0(7)	3655.2(4)	37(1)*
N(1)	669(2)	2505(5)	2247(3)	45(2)*
N(2)	1428.0(14)	945.3(45)	2402.7(27)	35(2)*
N(3)	1804(2)	2512(5)	3872(3)	36(2)*
N(4)	1036(2)	4034(5)	3623(3)	43(2)*
C(1)	638(2)	1168(6)	1850(4)	41(2)*
C(2)	241(2)	568(8)	1454(4)	54(2)*
C(3)	234(2)	-750(8)	1087(4)	61(3)*
C(4)	612(3)	-1507(7)	1144(4)	57(3)*
C(5)	1011(2)	-966(6)	1561(4)	50(2)*
C(6)	1023(2)	374(6)	1905(3)	40(2)*
C(7)	1698(2)	1722(6)	2014(3)	38(2)*
C(8)	1653(2)	1709(7)	1042(3)	56(3)*
C(9)	2013(2)	2638(6)	2475(3)	41(2)*
C(10)	2003(2)	3167(6)	3305(4)	37(2)*
C(11)	2211(2)	4587(7)	3520(4)	58(3)*
C(12)	1686(2)	3268(6)	4594(3)	37(2)*
C(13)	1939(2)	3125(7)	5413(4)	52(2)*
C(14)	1810(2)	3794(7)	6112(4)	58(3)*
C(15)	1424(2)	4552(7)	5992(4)	57(3)*
C(16)	1166(2)	4683(6)	5176(4)	53(3)*
C(17)	1298(2)	4054(6)	4469(4)	41(2)*
C(18)	836(2)	5126(7)	3211(4)	51(3)*
C(19)	905(3)	6613(7)	3544(5)	81(3)*
C(20)	562(2)	4952(6)	2396(4)	46(2)*
C(21)	475(2)	3710(7)	1930(4)	43(2)*
C(22)	173(2)	3769(8)	1062(4)	64(3)*
C(23)	2059(2)	-791(7)	3853(4)	53(2)*
C(24)	1019(2)	361(6)	4101(4)	47(2)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Atom coordinates ($\times 10^4$) and isotropic thermal parameters ($A^2 \times 10^3$)

$MeGa(C_{22}H_{21}N_4)$

Space group PT was assumed and shown to be correct by satisfactory refinement.

Figure 2 shows a view of the unit cell of $MeGa(C_{22}H_{22}N_4)$ and Figure 3 shows the orientation of one molecule within it.

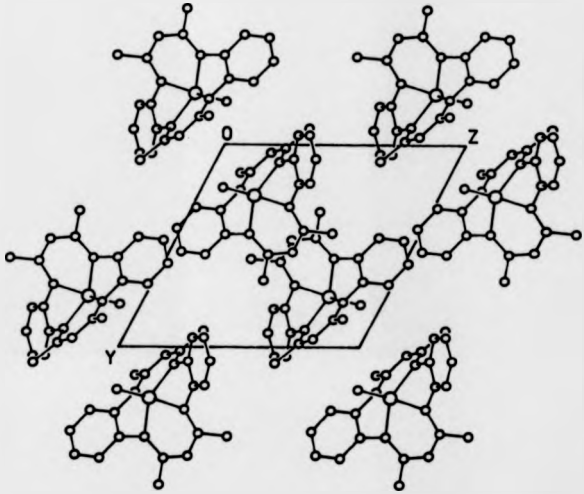


Figure 2 The unit cell of $MeGa(C_{22}H_{21}N_4)$

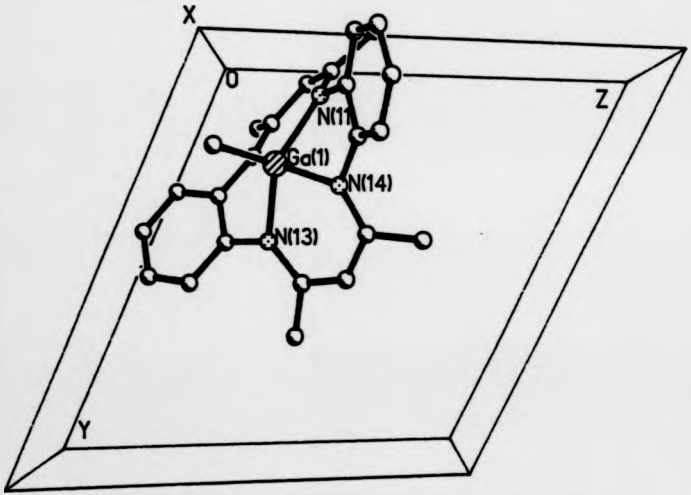


Figure 3 The orientation of one molecule in the unit cell of $MeGa(C_{22}H_{22}N_4)$

Table 10 Bond lengths for MeGa($C_{22}H_{22}N_4$) (Å)

Ga(1)-N(11)	2.023(5)	Ga(1)-N(12)	2.022(5)
Ga(1)-N(13)	2.005(5)	Ga(1)-N(14)	2.015(4)
Ga(1)-C(30)	1.958(8)	N(11)-C(2)	1.329(8)
N(11)-C(11)	1.401(8)	N(12)-C(4)	1.335(8)
N(12)-C(21)	1.403(9)	N(13)-C(7)	1.334(5)
N(13)-C(26)	1.415(8)	N(14)-C(9)	1.344(6)
N(14)-C(12)	1.396(9)	C(1)-C(2)	1.505(11)
C(2)-C(3)	1.404(10)	C(3)-C(4)	1.401(10)
C(4)-C(5)	1.500(10)	C(6)-C(7)	1.500(10)
C(7)-C(8)	1.378(9)	C(8)-C(9)	1.389(9)
C(9)-C(10)	1.500(9)	C(11)-C(12)	1.420(6)
C(11)-C(16)	1.381(10)	C(12)-C(13)	1.389(10)
C(13)-C(14)	1.381(11)	C(14)-C(15)	1.377(7)
C(15)-C(16)	1.390(11)	C(21)-C(22)	1.384(9)
C(21)-C(26)	1.396(7)	C(22)-C(23)	1.377(13)
C(23)-C(24)	1.355(9)	C(24)-C(25)	1.391(11)
C(25)-C(26)	1.377(11)		

Table 11 Bond angles for MeGa($C_{22}H_{22}N_4$) (°)

N(11)-Ga(1)-N(12)	89.6(2)	N(11)-Ga(1)-N(13)	143.8(2)
N(12)-Ga(1)-N(13)	78.7(2)	N(11)-Ga(1)-N(14)	78.8(2)
N(12)-Ga(1)-N(14)	141.4(2)	N(13)-Ga(1)-N(14)	89.3(2)
N(11)-Ga(1)-C(30)	108.6(3)	N(12)-Ga(1)-C(30)	108.2(2)
N(13)-Ga(1)-C(30)	107.7(3)	N(14)-Ga(1)-C(30)	110.4(3)
Ga(1)-N(11)-C(2)	127.5(5)	Ga(1)-N(11)-C(11)	106.4(4)
C(2)-N(11)-C(11)	125.1(6)	Ga(1)-N(12)-C(4)	128.4(5)
Ga(1)-N(12)-C(21)	106.5(4)	C(4)-N(12)-C(21)	124.8(6)
Ga(1)-N(13)-C(7)	128.2(5)	Ga(1)-N(13)-C(26)	106.5(3)
C(7)-N(13)-C(26)	124.6(6)	Ga(1)-N(14)-C(9)	128.0(5)
Ga(1)-N(14)-C(12)	106.9(3)	C(9)-N(14)-C(12)	124.5(5)
N(11)-C(2)-C(1)	120.9(6)	N(11)-C(2)-C(3)	122.6(6)
C(1)-C(2)-C(3)	116.5(6)	C(2)-C(3)-C(4)	129.2(6)
N(12)-C(4)-C(3)	121.7(6)	N(12)-C(4)-C(5)	122.5(6)
C(3)-C(4)-C(5)	115.6(6)	N(13)-C(7)-C(6)	121.4(5)
N(13)-C(7)-C(8)	121.8(6)	C(6)-C(7)-C(8)	116.7(4)
C(7)-C(8)-C(9)	130.6(4)	N(14)-C(9)-C(8)	121.0(5)
N(14)-C(9)-C(10)	121.0(6)	C(8)-C(9)-C(10)	117.8(5)
N(11)-C(11)-C(12)	114.0(5)	N(11)-C(11)-C(16)	126.1(4)
C(12)-C(11)-C(16)	119.2(6)	N(14)-C(12)-C(11)	114.2(5)
N(14)-C(12)-C(13)	126.4(5)	C(11)-C(12)-C(13)	118.9(6)
C(12)-C(13)-C(14)	121.0(5)	C(13)-C(14)-C(15)	119.8(7)
C(14)-C(15)-C(16)	120.3(7)	C(11)-C(16)-C(15)	120.7(5)
N(12)-C(21)-C(22)	126.4(5)	N(12)-C(21)-C(26)	114.5(5)
C(22)-C(21)-C(26)	118.6(6)	C(21)-C(22)-C(23)	120.5(5)
C(22)-C(23)-C(24)	120.8(8)	C(23)-C(24)-C(25)	119.9(8)
C(24)-C(25)-C(26)	119.8(6)	N(13)-C(26)-C(21)	113.9(6)
N(13)-C(26)-C(25)	125.3(5)	C(21)-C(26)-C(25)	120.3(6)

Table 12 Atomic co-ordinates for $MeGa(C_{22}H_{22}N_4)$

Atom	x	y	z	U
Ga(1)	4943.1(8)	2509.8(6)	2352.8(5)	34(1)*
N(11)	4226(6)	864(4)	2658(4)	36(2)*
N(12)	2455(6)	2234(4)	1659(4)	36(2)*
N(13)	5254(6)	4396(4)	2983(4)	40(2)*
N(14)	6993(6)	3062(4)	4041(4)	35(2)*
C(1)	2510(9)	-812(7)	3170(6)	52(3)*
C(2)	2710(7)	184(5)	2608(5)	39(3)*
C(3)	1253(7)	405(5)	2109(5)	39(2)*
C(4)	1109(7)	1364(6)	1670(5)	41(3)*
C(5)	-615(7)	1402(7)	1301(6)	49(3)*
C(6)	6125(9)	6690(6)	4566(6)	50(3)*
C(7)	6284(7)	5406(5)	4181(5)	36(2)*
C(8)	7464(7)	5295(5)	5150(5)	40(2)*
C(9)	7822(7)	4222(5)	5136(5)	37(2)*
C(10)	9057(9)	4366(7)	6408(6)	57(3)*
C(11)	9735(7)	715(5)	3177(5)	36(3)*
C(12)	7265(7)	1935(5)	3950(5)	35(2)*
C(13)	8858(8)	1901(6)	4394(5)	41(3)*
C(14)	8967(9)	705(6)	4109(6)	49(3)*
C(15)	7484(9)	-475(6)	3328(6)	50(3)*
C(16)	5876(8)	-469(6)	2849(6)	44(3)*
C(21)	2415(7)	3240(5)	1264(5)	37(3)*
C(22)	1110(9)	3115(7)	179(6)	55(3)*
C(23)	1325(11)	4136(7)	-189(7)	68(4)*
C(24)	2823(10)	5275(7)	491(7)	74(4)*
C(25)	4168(9)	5419(6)	1571(6)	56(3)*
C(26)	3950(8)	4420(6)	1972(5)	43(3)*
C(30)	5539(9)	2115(6)	869(6)	50(3)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Atom coordinates ($\times 10^4$) and isotropic thermal parameters ($A^2 \times 10^3$)

$Me_2InI.TMEDA$

Systematic reflection conditions Okl, l=2n; hkO, h+k=2n indicating space group either Pcmn (non-standard setting of Pnma) or $Pc2_1n$ (non-standard setting of $Pna2_1$). Initially, the first was chosen, the likely value of Z requiring the molecule to lie on the mirror plane. Structure solution by SHELXTL/TREF) showed the In and I atoms. The light atoms were found by successive Fourier synthesis. Refinement proceeded to R = 0.08, but was unsatisfactory, the light atoms having very high thermal parameters. Conversion to $Pc2_1n$, with no constraints on the molecular symmetry allowed refinement to a final R of 0.046. However, the atoms in the $(CH_2)_2$ group had an implausibly small C-C distance (1.2Å) and, again, high thermal parameters. An alternative model was therefore adopted, in space group Pcmn, with a molecular mirror plane but with these atoms disordered across it and with their C-C distance constrained to 1.54(5)Å. Refinement then converged at a slightly higher R-value, (0.051), but it is considered that the model gives a more accurate impression of the real molecular geometry. The highly anisotropic thermal motion of C(2) and C(5) suggest that they also share in the disorder, but to a lesser extent that is difficult to model.

Table 13 Bond lengths for $Me_2InI.TMEDA$ (Å)

In-I	3.183(4)	In-N(1)	2.527(11)
In-N(2)	2.328(11)	In-C(1)	2.119(10)
N(1)-C(4)	1.451(26)	N(1)-C(5)	1.399(17)
N(2)-C(2)	1.454(17)	N(2)-C(3)	1.489(25)
C(3)-C(4)	1.490(37)		

Table 14 Bond angles for $Me_2InI.TMEDA$ (°)

I-In-N(1)	164.4(2)	I-In-N(2)	89.8(3)
N(1)-In-N(2)	74.6(4)	I-In-C(1)	90.5(3)
N(1)-In-C(1)	94.4(3)	N(2)-In-C(1)	108.8(4)
I-In-C(1a)	90.5(3)	N(1)-In-C(1a)	94.4(3)
C(1)-In-C(1a)	142.4(7)	In-N(1)-C(4)	102.6(12)
In-N(1)-C(5)	112.9(8)	C(4)-N(1)-C(5)	93.4(13)
C(4)-N(1)-C(4a)	34.1(18)	C(5)-N(1)-C(5a)	110.9(16)
In-N(2)-C(2)	110.8(7)	In-N(2)-C(3)	108.6(9)
C(2)-N(2)-C(3)	97.1(16)	C(2)-N(2)-C(2a)	107.4(14)
C(3)-N(2)-C(3a)	28.2(30)	N(2)-C(3)-C(4)	109.8(22)
N(1)-C(4)-C(3)	110.4(19)		

Position a: x, 1.5-y, z

Table 15 Atomic co-ordinates for $Me_2InI.TMEDA$

Atom	x	y	z	U
In	1278.8(9)	7500.0	1778.7(7)	47(1)*
I	4235.2(12)	7500.0	2630.2(12)	102(1)*
N(1)	-1205(11)	7500	1639(8)	53(4)*
N(2)	518(12)	7500	3535(8)	63(4)*
C(1)	1485(11)	5661(9)	1260(11)	75(4)*
C(2)	989(17)	6425(15)	4108(11)	111(6)*
C(3)+	-904(20)	7167(37)	3533(16)	90(18)*
C(4)+	-1609(26)	7890(20)	2699(19)	95(11)*
C(5)	-1700(15)	8556(13)	1147(17)	127(7)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

+ Occupancy 0.5.

Atom coordinates ($x10^4$) and isotropic thermal parameters ($Å^2x10^3$)

APPENDIX D

Experimental

APPENDIX D. Experimental

GENERAL EXPERIMENTAL

Most of the products are moisture sensitive and were therefore handled using vacuum line, Schlenck line and glove box techniques. Solvents were dried and distilled under nitrogen before use. Tetrahydrofuran, diethylether, toluene benzene, n-hexane and n-pentane were dried over sodium/benzophenone or sodium/potassium eutectic alloy. N.M.R. solvents were stored over 3Å molecular sieves.

Routine ^{1}H N.M.R. spectra were run on a Perkin Elmer R34 (220 MHz) spectrometer. Additional ^{1}H, and ^{13}C and ^{31}P spectra were run on a Bruker WH400 instrument. Spectra recorded at Octel were obtained using a Bruker AC200 machine. Chemical shifts are quoted relative to tetramethylsilane (T.M.S.) although dichloromethane (δ = 5.34 p.p.m. in $CDCl_3$) was the most frequently used reference standard because it does not obscure aromatic, aliphatic or organometallic resonances.

Infra-red spectra were run on a Perkin-Elmer 580B spectrophotometer using caesium iodide plates.

Elemental analyses were carried out by the Analytical Department at Octel. Carbon, hydrogen, nitrogen analyses were determined using a Perkin Elmer 2400. D.T.A. and D.T.G. results were obtained using a Stanton Redcroft STA 1000.

Trimethylgallium, anhydrous gallium(III)chloride and indium metal were obtained from Johnson Matthey. Gallium metal was obtained from Johnson Matthey and Aldrich. The trimethylgallium (b.p 56°C) was stored in a cylinder attached to the vacuum line.

EXPERIMENTAL (Chapter 2)

N,N′-diphenylformamidine, N,N′-dicyclohexyl-4-morpholine-carboxamidine, benzamidine hydrochloride hydrate and acetamidine hydrochloride were obtained from Aldrich. N,N′-diphenylbenzamidine was obtained from Lancaster Synthesis. All other amidines were supplied by our collaborating body, Octel, except for N,N′-dicyclohexylacetamidine which was prepared as described later.

The N-substituted amidines are soluble in moderately polar organic solvents such as toluene, dichloromethane, acetone and propan-2-ol but only slightly so in short chain alkanes, ethanol and water. Primary amidines are soluble in polar solvents but are hygroscopic and decomposed by water. Solubilities increase very markedly with temperature. The dimethylgallium derivatives are considerably more soluble in hexane than the parent amidines.

Preparation of Dimethylgallium - N,N′-diphenylbenzamidine

This and all other preparations involving trimethylgallium were performed on a vacuum line. N,N′-diphenylbenzamidine (0.93g; 3.4 mmol) was placed in a round-bottomed flask with about 30 cm^3 of dry toluene. A slight excess of Me_3Ga was weighed out in a calibrated gas flask. The amidine solution was degassed by repeated solidification and fusion under vacuum. The Me_3Ga was condensed on the solution at -196°C, and the stirred mixture allowed to warm slowly to room temperature to give a yellow solution. The approximate volume of methane evolved was measured using a calibrated portion of the vacuum line, and the solvent and excess Me_3Ga distilled off. The product is a slightly yellowish solid which sublimes slowly at about 100°C under vacuum, rapidly near 130°C. Yield, 1.01g (79%). Analysis, calculated for $C_{21}H_{21}N_2Ga$ (M.W. 371.13): C, 67.96; H, 5.70; N, 7.55%. Found: C, 67.00; H, 5.61; N, 7.43%. N.M.R. ($CDCl_3$): δ_H -0.27 (= 1.5 H, s, $GaCH_3$), 0. 00 (= 4.5H, s, $GaCH_3$), 6.60-7.45 (15 H, 4 x m, C_6H_5).

Crystals of this compound suitable for X-ray diffraction were grown by preparing this compound in n-hexane with a considerable excess of Me_3Ga. The reaction mixture was cooled to -35°C for three days and the solvent removed at that temperature.

Preparation of Dimethylgallium-N,N′-di(p-chlorophenyl) acetamidine.

The preparation used was similar to that used for the N,N′-diphenylbenzamidine complex. The product is a white solid which sublimes fairly rapidly at 120°C under vacuum. At atmospheric pressure it melts with decomposition above 90°C. This and other acetamidine complexes were found to crystallise as small needles, too fine for X-ray diffraction. Yield, 0.99g (63%). Analysis, calculated for $C_{16}H_{17}N_2GaCl_2$ (M.W. 377.95): C, 50.85; H, 4.53; N, 7.41%. Found: C, 50.74; H, 4.41; N, 7.28%. N.M.R. ($C_6D_5CD_3$): δ_H -0.15, -0.11 (≈ 1.5H, 2 x s, $GaCH_3$). 0.11 (≈ 4.5H, s, $GaCH_3$), 1.42 (3H, s, CH_3), 6.61 (4H, d, C_6H_4) 7.12 (4H, d, C_6H_4).

Preparation of Dimethylgallium - N,N′ -diphenylformamidine

Before use the amidine was recrystallised from methanol to give pale pink needles and dried under vacuum. The Me_3Ga was measured out as a liquid (density 1.12-1.13g cm^{-3}) for this and subsequent rections, using the $2cm^3$ capacity "calibrated cold-finger" device illustrated below. Alternatively, the device can be weighed. Procedure during first preparation otherwise as for the N,N′-diphenylbenzamidine complex. Removal of the toluene proved difficult so n-hexane was used subsequently for the preparation of this compound. The reaction goes to completion despite the low solubility of the amidine, as the product is more soluble. Yield, 0.97g (75%). Analysis, calculated for $C_{15}H_{17}N_2Ga$ (M.W. 295.03). C, 61.07; H, 5.81; N, 9.50%. Found: C, 59.25; H, 5.83; N, 9.26%. N.M.R. ($CDCl_3$): δ_H -0.28, to -0.23 (6H, 3 x s, $GaCH_3$), 7.10, 7.35 (10H, 2 x m, C_6H_5), 8.25 (1H, s, CH).

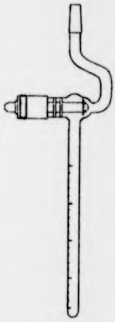


Figure 1. Calibrated cold finger device used for measuring out liquid trimethylgallium.

Preparation of Dimethylgallium - N,N′-diphenylacetamidine

Again the procedure was similar to that used for N,N′-diphenylbenzamidine complex, except that n-hexane was used as solvent. All other dimethylgallium-amidine compounds described below were prepared using this procedure unless stated otherwise. The product is a white solid. Yield, 1.08g (71%). Analysis, calculated for $C_{16}H_{19}N_2Ga$ (M.W. 309.06). C, 62.18; H, 6.20; N, 9.06%. Found: C, 62.55; H, 6.05; N, 8.87%. N.M.R. ($CDCl_3$) δ_H -0.47 (= 2H, s, $GaCH_3$), -0.07 (= 4H, 2 x s, $GaCH_3$), 2.10 (3H, s, CH_3) 7.05, 7.33 (10H, 2 x m, C_6H_5).

Preparation of Dimethylgallium - N,N′-di(p-tolyl)benzamidine)

Since the method has already been described only the details of the product are given hereafter. Pale yellow solid, yield, 1.10g (74%). Analysis, calculated for $C_{23}H_{25}N_2Ga$. (M.W. 399.18): C, 69.20; H, 6.31; N, 7.02%.

Found: C, 69.87; H, 6.29; N, 7.07%. N.M.R. ($CDCl_3$) δ_H -0.28 (= 1.5H, s, $GaCH_3$), 0.00 (= 4.5H, s, $GaCH_3$), 6.60 (4H, d, C_6H_4) 6.95 (4H, d, C_6H_4), 7.35 (5H, m, C_6H_5).

Preparation of Dimethylgallium - N,N′-di(p-tolyl)acetamidine

The product is a white solid. Yield, 0.56g (88%). Analysis, calculated for $C_{18}H_{23}N_2Ga$ (M.W. 337.11): C, 64.13; H, 6.88; N, 8.31%. Found: C, 65.46; H, 6.82; N, 8.87%. N.M.R. ($CDCl_3$)δ_H -0.50 (= 1H, s, $GaCH_3$), -0.08 (= 5H, s, $GaCH_3$), 2.10 (3H, s, CH_3), 2.33 (6H, s, CH_3), 6.93 (4H, d, C_6H_4), 7.15 (4H, d, C_6H_4).

Preparation of Dimethylgallium-N,N′-di(p-fluorophenyl)acetamidine

Colourless crystalline solid. Yield, 1.8g, (89%). Analysis, calculated for $C_{16}H_{17}N_2GaF_2$ (M.W. 345.04): C, 55.70; H, 4.97; N, 8.12%. Found: C, 55.77; H, 4.86; N, 7.96%. N.M.R. ($CDCl_3$)δ_H -0.45 (= 0.5H, 2 x s, $GaCH_3$), -0.04 = 5.5H, s, $GaCH_3$), 2.07 (3H, s, CH_3), 6.90 - 7.10(10H, m, C_6H_4).

Preparation of Dimethylgallium -N,N′-dicyclohexyl-4-morpholine carboxamidine.

Colourless crystalline solid. Yield, 1.48g (96%). Analysis, calculated for $C_{19}H_{36}N_3OGa$ (M.W. 392.23): C, 58.18; H, 9.25; N, 10.71%. Found: C, 57.36, H, 9.32; N, 10.17%. N.M.R. ($CDCl_3$), δ_H -0.41 (= 0.5H, 2 x s, $GaCH_3$), -0.33 (= 5.5H, s, $GaCH_3$), 0.95 - 1.35, 1.50 - 1.90 (20H, 2 x m, CH_2) 3.06 (2H, m, CH), 3.24 (4H, tr, CH_2), 3.73 (4H, tr, CH_2).

Preparation of Dimethylgallium-N,N′-dicyclohexylacetamidine

The amidine was prepared by the reaction of dicyclohexylcarbodiimide with methyl lithium. Dicyclohexylcarbodiimide (2.65g, 12.85 mmole) was dissolved in 50 cm^3 diethylether. To this was added a solution of methyl lithium,

also in diethylether (10 cm^3, 15 mmol). The reaction mixture was left stirring for about two hours before distilled water (10 cm^3) was added cautiously. The ether layer was washed with a further 10 cm^3 of water. After separating, the ether was removed under vacuum to give an oil. This was redissolved in ether (2 cm^3) and the solution transferred to a sublimer. The ether was removed again at room temperature and the oil heated. A white solid sublimes rapidly at 100°C. the ^1H n.m.r. spectrum consists of a rather uninformative mass of peaks. Yield, 2.06g (72%). Analysis, calculated for $C_{14}H_{26}N_2$ (M.W. 222.38): C, 75.62; H, 11.79; N, 12.60%. Found: C, 75.70; H, 11.63; N, 11.82%. N.M.R. ($CDCl_3$) δ_H 1.00 - 1.95, 1.77, 1.96 (23H, 2 x m, 2 x s, CH_2 + CH_3) 2.75 - 2.95, 3.10 - 3.45 (2H, 2 x m, CH).

The dimethylgallium compound was prepared by the general method except that no solvent was used as even n-hexane proved difficult to remove from this product. The reaction mixture liquifies before finally setting solid. Yield, 1.07g (95%). Analysis, calculated for $C_{16}H_{31}N_2Ga$ (M.W. 321.15): C, 59.84; H, 9.73; N, 8.72%. Found; C, 61.34; H, 9.66; N, 8.95%. N.M.R. ($CDCl_3$) δ_H - 0.31 (6H, s, Ga) 0.95 - 1.80 (20H, 2 x m, CH_2), 1.87 (3H, s, CH_3), 3.05 - 3.25 (2H, m, CH).

Preparation of Dimethylgallium-benzamidine

Attempts were made to prepare pure benzamidine from its hydrated hydrochloride salt using aqueous potassium hydroxide and extracting the amidine with dichloromethane,[250] but this produced an impure product. A better sample was prepared by dissolving 1.42g (62 mmole) sodium in methanol, and adding 9.65g (61 mmole) benzamidine hydrochloride hydrate. This was left to stir for one hour before the solvent was removed under vacuum and a cold finger inserted. Benzamidine sublimed fairly quickly at 80°C. Yield, 5.20g (70%). The amidine was re-sublimed before use. N.M.R. ($CDCl_3$) δ_H 7.35 (3H, s, NH, $CHCl_3$, 7.50 (3H, m, C_6H_5), 7.68 (2H, m, C_6H_5). The singlet at 7.35

p.p.m. is probably due to proton deuterium exchange between $CDCl_3$ and the amidine. This has been reported to occur with acetamidine.[251]

The dimethylgallium derivative was again prepared in the absence of solvent, to give a foamy solid. Yield, 0.42g (58%). Analysis, calculated for $C_6H_{13}N_2Ga$ (M.W. 218.94): C, 49.37; H, 5.98; N, 12.80%. found: C, 49.63; H, 6.00; N, 12.11%. N.M.R. ($C_6D_5CD_3$) δ_H - 0.27 (6H, s, $GaCH_3$) 4.63 (1H,br.s, NH ?), 5.88 (1H, br.s, NH ?), 7.10 (3H, m, C_6H_5), 7.35 (2H, m, C_6H_5).

Preparation of Dimethylgallium-acetamidine

The amidine was prepared by heating the hydrochloride salt (2.77g, 29 mmole) with potassium hydroxide (approximately 8g, 140 mmoles of ground-up pellets) at 120°C under vacuum so the amidine sublimes out of the reaction mixture. Yield, 1.32g (78%). The white solid was re-sublimed under vacuum at about 50°C before use. It has been prepared previously from the hydrochloride using sodium methoxide in methanol.[251] This amidine is particularly hygroscopic liquifying completely after perhaps ten seconds exposure to air. Analysis, calculated for $C_2H_6N_2$ (M.W. 58.08): C, 41.36; H, 10.41; N, 48.23%. Found: C, 41.95; H, 10.17; N, 47.30%. N.M.R. ($CDCl_3$) δ_H 1.98 (3H, s, CH_3), 7.36 (3H, s, NH/$CHCl_3$). This spectrum is in reasonable agreement with that reported by Crosland and Grevil,[251] who noted that proton-deuterium exchange occurs between the amidine and $CDCl_3$.

The dimethylgallium derivative was prepared by the usual method. The product is a white solid. Yield, 0.40g (57%). Analysis, calculated for $C_4H_{11}N_2Ga$ (M.W. 156.87): C, 30.63; H, 7.07; N, 17.86%. Found: C, 31.53; H, 7.36; N, 16.24%. N.M.R. ($CDCl_3$) δ_H - 0.46 (6H, s, $GaCH_3$), 1.99 (3H, s, CH_3), 7.34 (2H, s, NH).

Preparation of Dichlorogallium-N,N′-di(p-chlorophenyl)acetamidine

Gallium(III)chloride (0.92g, 5.23 mmol) was mixed with N,N′-di(p-chlorophenyl)acetamidine (4.36g, 15.62 mmol) heated to 140°C for about two hours melting both $GaCl_3$ and amidine. A whitish solid soon formed and settled beneath the liquid. This did not melt, even when the reaction mixture was heated to 180°C. On cooling the whole reaction mixture set solid. The large excess of unreacted amidine was removed by washing with toluene. The product is soluble only in acetone and tetrahydrofuran and could not be recrystallised.

With equivalent reactions using only one and two equivalents of amidine an appropriately smaller amount of excess amidine remained, supporting the conclusion drawn from analytical and mass spectral data that only one equivalent of hydrogen chloride is evolved. Yield, 0.56g (26%). analysis, calculated for $C_{14}H_{11}N_2GaCl_4$ (M.W. 418.79): C, 40.15; H, 2.65; N, 6.69%. Found: C, 40.04; H, 2.42; N, 6.09%.

Preparation of Gallium(III)chloride-N,N′-di(p-chlorophenyl)acetamidine

Solutions of $GaCl_3$ (1.02g, 5.79 mmol in about 30 ml toluene) and N,N′-di(p-chlorophenyl)acetamidine (0.67g, 5.98 mmol, toluene 30 ml) were mixed and warmed. At about 40°C, a thick white precipitate appeared. On refluxing at 130 - 140°C (under a positive presure of nitrogen) for 1 hour the precipitate dissolved, but quickly reappeared on cooling. The product was filtered off and washed with warm toluene (50 cm^3). Yield, 2.12g (80%). Analysis, Calculated for $C_{14}H_{12}N_2GaCl_5$ (M.W. 455.252): C, 36.94; H, 2.66; N, 6.15; Cl, 38.94%. Found: C, 36.66; H, 2.62; N, 5.79; Cl, 38.78%. N.M.R. (CD_3COCD_3) δ_H 2.42 (3H, s, CH_3) 7.52 (8H, s, C_6H_4) 10.36 (1H, br.s, NH). $\delta^{13}C$ 18.95 (CH_3), 127.88 (CH), 130.73 (CH), 133.74 (CCl) 136.48 (CN) 164.44 (NCN).

Preparation of Gallium(III)chloride-N,N′-diphenylacetamidine

Procedure as for the previous compound. The cream coloured precipitate dissolved at 110°C, and did not reappear until the temperature of the solution had dropped to about 40°C. Yield, 16.36g (91%). Analysis, calculated for $C_{14}H_{14}N_2GaCl_3$ (M.W. 386.36): C, 43.52; H, 3.65; N, 7.25; Cl, 27.53%. Found: C, 42.67; H, 3.44; N, 7.25; Cl, 27.28%. N.M.R. (CD_3COCD_3) δ_H 2.39 (3H, s, CH_3), 7.35 7.48 (10H, 2 x m, C_6H_5), 10.28 (1H, br.s, NH) δ ^{13}C 18.83 (CH_3) 125.85 (CH), 128.25 (p-CH), 130.52 (CH), 138.02 (CN), 163.46 (NCN).

Table 1. Infra-red data for the dimethylgallium-amidine complexes and gallium(III)chloride-N,N'-di(p-chlorophenyl)acetamidine.

Complex	Infra-red bands
[PhNC(Ph)NPh]$GaMe_2$	1625(s), 1588(s), 1577(m), 1540(m), 1490(s), 1445(s), 1441(s), 1425(w-m), 1335(w-m), 1225(w), 1210(w), 1028(w), 922(w), 780(w), 760(w), 745(w), 701(s), 592(w, br), 570(w, br), 530(w).
[PhNC(Me)NPh]$GaMe_2$	1660(w), 1635(s), 1588(s), 1542(m), 1520(s, br), 1495(s), 1445(m), 1420(s), 1380(w), 1334(w), 1225(m), 1075(w), 800(m), 750(m), 705(s), 590(m, br), 580(m, br), 530(w, br), 520(w, br).
[(p-ClPh)NC(Me)N(p-ClPh)]$GaMe_2$	1625(s), 1587(s), 1540(s), 1515(s), 1490(s), 1400(m), 1335(m), 1230(m), 1220(m), 1092(m), 1015(m), 870(w), 845(m), 820(m), 580(w-m, br), 525(w-m, br), 500(w-m).
[(p-ClPh)NC(Me)N(p-ClPh)]$GaCl_3$	3300(w), 3290(s), 1635(s), 1598(s), 1582(s), 1570(s), 1485(s), 1400(w), 1258(w), 1090(s), 1012(s), 985(m), 872(w-m), 850(w), 820(m), 795(m), 735(w), 718(m), 698(m), 623(m), 615(m), 520(w), 495(s), 400(s), 375(s), 350(s).
[PhNC(H)NPh]$GaMe_2$	1680(m), 1660(s), 1605(s), 1588(s), 1562(s), 1490(s), 1375(s), 1230(s), 1210(s), 1172(w-m), 1030(w-m), 980(w-m, br), 760(s), 700(s), 575(m), 530(m), 490(w).

EXPERIMENTAL (Chapter 3)

Preparation of 5,7,12,14-Tetramethyldibenzo [b,i]1,4,8,11-tetraazacyclotetradecine, H_2tmtaa.

H_2tmtaa was prepared by the standard method based[226] on the reactions below:

$$2o\text{-}(H_2N)_2C_6H_4 + 2CH_3COCH_2COCH_3 + Ni(CH_3CO_2)_2\,4H_2O \xrightarrow[CH_3OH]{} Ni(C_{22}H_{22}N_4) + 2CH_3CO_2H + 8H_2O$$

$$Ni(C_{22}H_{22}N_4) + 4HCl \xrightarrow[C_2H_5OH]{} [C_{22}H_{26}N_4][NiCl_4]$$

$$[C_{22}H_{26}N_4][NiCl_4] + 2NH_4PF_6 \xrightarrow[H_2O]{} [C_{22}H_{26}N_4][PF_6]_2 + 2NH_4Cl + NiCl_2$$

$$[C_{22}H_{26}N_4][PF_6]_2 + 2N(C_2H_5)_3 \xrightarrow[CH_3OH]{} C_{22}H_{24}N_4 + 2HN(C_2H_5)_3\,PF_6$$

The ^{1}H N.M.R. spectrum showed the product to contain ethanol which was still present after pumping under vacuum for several hours. It was removed by dissolving the yellow powder (with difficulty) in refluxing toluene. After approximately two hours the solution was allowed to cool. Only a small quantity of product crystallised, so the toluene was removed under vacuum leaving a honey-coloured powder. Yield (ethanol free) 1.12g (19%). Analysis, calculated for $C_{22}H_{24}N_2$ (M.W. 344.46): C, 76.71; H, 7.02; N, 16.27%. Found: C, 77.02; H, 7.08; N, 15.78%. N.M.R. ($CDCl_3$): δ_H 2.13 (12H, s, CH_3), 4.87 (2H, s, CH), 6.98 (8H, s, C_6H_4) 12.57 (2H, s, NH).

Preparation of $Me_2GaHtmtaa$

The procedure used was similar to that for the dimethylgallium-amidine complexes. Thus H_2tmtaa (0.51g, 1.48 mmol) was partially dissolved in n-hexane ($20cm^3$) and Me_3Ga (0.20g, 1.76 mmol) was condensed on to the mixture under vacuum at -196°C. On warming the solution methane evolution commenced just

below room temperature. A pale yellow solid formed slowly with a reddish brown supernatant solution. The solvent was syringed off and the product washed twice with n-hexane (2 x $3cm^3$). The product was then dried by pumping under vacuum. Yield, 0.49g, (75%). Analysis, calculated for $C_{24}H_{29}N_4Ga$ (M..W. 443.25): C, 65.04; H, 6.60; N, 12.64%. Found: C, 64.25; H, 6.62; N, 12.25%. N.M.R. ($CDCl_3$): δ_H -1.15, -0.38 (2 x 3H, s, $GaCH_3$), 1.64, 2.09 (2 x 6H, s, CH_3) 4.79, 4.94 (2 x 1H, s, CH), 6.98-7.13 (8H, m, C_6H_4), 12.43 (1H, s, NH).

The crystals used in the X-ray diffraction study were grown by slow evaporation of solvent from a toluene/n-hexane solution.

Preparation of MeGatmtaa

The dimethylgallium complex, $Me_2GaHtmtaa$ (0.17g, 0.38 mmol) was heated carefully under about 2cm nitrogen pressure to prevent sublimation. T.G.A. and D.T.A. results (Chapter 3) showed that this conversion occurs at about 220°C. While this can be achieved under controlled conditions, in practice it was convenient to heat with a hot air gun until the powder turned red and in places started to melt. ^1H N.M.R. and elemental analysis showed this product to be acceptably pure without further treatment. Yield, 0.11g (67%). Analysis, calculated for $C_{23}H_{25}N_2Ga$ (M.W. 427.20): C, 64.67; H, 5.90; N, 13.12%. Found: C, 64.12; H, 5.79; N, 12.91%. N.M.R. ($CDCl_3$): δ_H -0.93 (3H, s, $GaCH_3$), 2.21 (12H, s, CH_3), 4.80 (2H, s, CH), 6.97-7.07 (8H, 2 x m, C_6H_4).

Orange crystals of this compound, suitable for X-ray diffraction, were grown from a toluene solution layered with n-pentane.

Table 2 Summary of Infra-red spectra (Nujol mull, CsI plates) of H_2tmtaa, Me_2GaHtmtaa and MeGatmtaa.

Compound	
H_2tmtaa	1620(s), 1590(w-m), 1552(s), 1510(m), 1365(s), 1292(m), 1272(m), 1185(m), 742(s), 732(s).
Me_2GaHtmtaa	3060(w), 1620(s), 1592(w-m), 1565(m), 1542(s), 1502(m), 1380(m), 1365(m), 1285(m), 1270(m), 1190(m), 1178(m), 1112(m), 1030(m), 1015(m), 795(m), 780(m), 742(s), 575(m), 535(m), 488(w).
MeGatmtaa	3060(w), 1572(m), 1562(s), 1538(s), 1480(s), 1420(s), 1370(m), 1280(m), 1198(s), 1035(m), 755(s), 748(s), 740(s), 565(m), 522(w).

EXPERIMENTAL (Chapter 4)

Triphenylphosphine, 1,1-bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane and N,N,N′,N′-tetramethylethylenediamine were purchased from Aldrich. The phosphines were used as received. TMEDA was dried using sodium-potassium eutectic alloy and distilled under vacuum before use. Triphenylarsine was kindly donated by Dr A.F. Hill. Dimethylindium iodide was prepared using the method of Worrall and Gynane.[136] Indium metal foil was reacted with methyl iodide at room temperature. Sublimation of a mixture of the resulting methylindium "sesquiiodide" and potassium iodide yielded dimethylindium iodide.

Preparation of $Me_2InI.PPh_3$

A solution of triphenylphosphine (0.31g, 1.18 mmol) in toluene (5 cm^3) was added over a period of about 5 minutes with stirring, to a toluene solution (25 cm^3) containing dimethylindium iodide (0.32g, 1.18 mmol). The very faint pinkish colour of the Me_2InI solution disappeared immediately. The solvent was removed under vacuum, leaving a crystalline white powder. Previous preparations have used diethylether as the solvent.[70,112] Yield, 0.47g (75%). Analysis, calculated for $C_{20}H_{21}PInI$ (M.W. 534.09): C, 44.98; H, 3.96%. Found: C, 44.90: H, 4.00%. N.M.R. ($CDCl_3$): δ_H 0.30 (5H, s, $InCH_3$), 7.50 (15H, m, C_6H_5). $^{31}P\{^1H\}$-N.M.R. ($C_6H_5CH_3/C_6D_5CD_3$): δ-11.55 p.p.m.

Preparation of $Me_2InI.(Ph_2P)_2CH_2$

Procedure much as for the previous compound. The reaction can also be performed by mixing the solid reactants and adding toluene (30 cm^3), filtering and removing the solvent to give a white solid. Yield, 0.12g (56%). Analysis,

calculated for $C_{27}H_{28}P_2InI$ (M.W. 656.19): C, 49.42; H, 4.30%. Found: C, 51.61; H, 4.02%. N.M.R. ($CDCl_3$): δ_H 0 28 (6H, s, $InCH_3$), 3.20 (2H, tr, CH_2), 7.2-7.6 (20H, m, C_6H_5). $^{31}P\{^1H\}$-N.M.R. ($C_6H_5CH_3/C_6D_5CD_3$): δ -22.45 p.p.m.

Preparation of $Me_2InI.(Ph_2P)_2(CH_2)_2$

Procedure as for the previous compound. The product is again a white powder. Yield, 0.56g (73%). Analysis, calculated for $C_{28}H_{30}P_2InI$ (M.W. 670.22): C, 50.18; H, 4.51%. Found: C, 52.11; H, 3.95%. N.M.R. ($CDCl_3$): δ_H 0.20 (6H, s, $InCH_3$), 2.37 (4H, s, CH_2), 7.45 (20H, s, C_6H_5). $^{31}P\{^1H\}$-N.M.R. ($C_6H_5CH_3/C_6D_5CD_3$): δ - 14.57.

Preparation of $Me_2InI.AsPh_3$

Method as for the previous compound. Yield, 0.12g (52%). Analysis, calculated for $C_{20}H_{21}AsInI$ (M.W. 578.04): C, 41.56; H, 3.66%. Found: C, 41.58; H, 3.31%. N.M.R. ($CDCl_3$): δ_H 0.77 (4H, s, $InCH_3$), 7.39 (15H, s, C_6H_5).

Preparation of $Me_2InI.(Me_2N)_2(CH_2)_2$

0.13g (0.48 mmol) of dimethylindium iodide was dissolved in toluene (30 cm^3). Approximately 0.2 cm^3 (0.15g, 1.33 mmol) of TMEDA was added. A coarse, colourless precipitate appeared immediately. This was washed with three 5 cm^3 portions of toluene and one of n-hexane. The granular solid was dried under vacuum. Yield, 0.06g (32%). Analysis, calculated for $C_8H_{22}N_2InI$ (M.W. 388.00): C, 24.76; H, 5.72; N, 7.22%. Found: C, 24.57; H, 5.57; N, 6.50. N.M.R. ($CDCl_3$): δ_H 0.30 (6H, s, $InCH_3$), 2.53 (12H, s, CH_3), 2.63 (4H, s, CH_2).

The crystals used for the X-ray diffraction study were grown by allowing TMEDA vapour to diffuse into a toluene solution of dimethylindium iodide, as shown below. Layering methods can be used but crystallisation is usually too rapid.

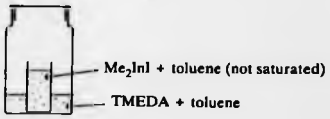


Figure 2. Method used to grow crystals of $Me_2InI.TMEDA$

Table 3 Summary of the infra-red spectra of the dimethylindium iodide adducts.

Compound	I.R. bands (cm^{-1}) nujol mull, CsI plates
$Me_2InI.PPh_3$	1480(m), 1438(s), 1310(w), 1182(w), 1160(w), 1098(m-s), 1028(w-m), 1000(w-m), 745(s), 725(m-s), 710(m-s), 695(s), 518(m-s) 497(m-s) 478(w), 435(w).
$Me_2InI.(Ph_2P)_2CH_2$	1485(m), 1435(s), 1356(w), 1103(w-m), 1028(w), 1000(w), 780(w-m), 762(w-m), 745(s), 736(s), 695(s), 525(w-m), 515(w-m), 500(w), 485(w-m), 480(w-m), 471(w).
$Me_2InI.(Ph_2P)_2(CH_2)_2$	1437(m), 1160(w), 1100(w), 1070(m), 1026(w), 1000(w), 751(w), 742(m), 728(s), 707(w), 692(s), 675(w), 515(m), 507(w), 477(m), 446(w).
$Me_2InI.AsPh_3$	3060(m), 1580(w), 1482(s), 1435(s), 1075(w), 1025(w), 1000(w), 735(s), 695(s), 552(w), 475(m), 312(m).
$Me_2InI.TMEDA$	1343(s), 1300(w), 1248(w), 1222(w), 1210(m), 1180(m), 1165(w), 1155(w), 1120(m), 1100(w), 1081(s), 1068(m), 1058(m), 1003(s), 847(s), 820(w), 785(s), 640(w), 582(m), 532(m), 505(w), 486(w).

APPENDIX E

Mass Spectra

APPENDIX E Mass Spectra

The mass spectra reported in this thesis were run by Mr I.K. Katyal (University of Warwick) using a Kratos MS-80 instrument. Samples of very air sensitive compounds were sealed in thin-walled glass capillaries under nitrogen which were broken open in air immediately before being introduced into the source. Deterioration of the sample sitting at the bottom of the capillary appears to be negligible.

The E.I. mass spectra were obtained at 70 electron volts. Ammonia was used for the chemical ionisation experiments.

Some gas-chromatography mass spectra were run at Octel on a Finnegan-MATT ITD system by Chris Blanden.

E.I. Mass Spectrum of $Me_2Ga[PhN=C(Ph)NPh]$

Measured Mass	% Int. Base
374.1644	4
373.1561	2 8
372.1462	12 7
371.1642	6 2
370.1349	18 8
369.1348	3 0
359.1244	1 0
358.1237	12 9
357.1227	57 4
356.1205	19 5
355.1143	77 9
354.1056	3
353.1277	4
343.2134	2 1
342.0499	1 1
341.0238	4 3
340.0873	9
339.0874	3 7
274.1440	3
273.1447	4 7
272.1397	23 3
271.1493	12 5
270.2477	2 1
269.1234	2 0
268.1091	6
267.1065	3
243.1085	1 1
239.0406	3
237.0244	5
195.1013	1 0
194.1031	1 5
193.0524	6
187.2894	3
182.1059	1 5
181.1035	21 9
180.0950	100 0
179.0883	1 1
178.0705	1 1
177.0402	8
169.0967	8
168.0893	2 0
167.0818	4 5
166.0841	7
164.0133	1 0
163.0046	12 0
162.0081	1 4
161.0049	18 6
154.0854	3
153.0733	1 0
152.0746	1 8
131.0658	9

Measured Mass	% Int. Base
149.0620	5
145.9771	3
145.0318	3
141.0773	4
140.0648	6
139.0581	3
136.0878	9
135.0737	1 0
134.0722	3
128.0618	1 2
127.0562	5
122.0669	5
116.0548	6
115.0508	6
105.0468	4
104.0510	1 5
103.0347	1 6
102.0415	4
100.9780	2 7
98.9792	4 2
93.0699	5
92.0595	1 3
91.0550	1 7
89.0410	4
85.9537	4
83.9438	6
81.0610	4
78.0357	3 4
77.0388	40 2
76.0240	1 6
75.0156	8
74.0134	6
70.9246	3 9
68.9400	6 5
66.0427	4
65.0385	2 5
64.0289	6
63.0323	9
52.0388	7
51.0248	8 5
50.0151	1 2
43.0189	3
39.0233	1 9
38.0159	3
31.9918	3
28.0052	1 1
27.0194	3

E.I. Mass Spectrum of $Me_2Ga[PhN=C(Me)NPh]$

Measured Mass	% Int Data
311	9
310	4 2
309	1 3
308	6 1
296	5 6
295	32 7
294	9 0
293	49 2
280	7
279	3 5
278	9
277	4 3
239	6
237	9
211	5 1
210	32 9
209	23 6
208	2 6
208	2 7
207	1 2
202	5
200	8
194	1 1
169	9
168	1 2
167	3 3
166	7
161	7
149	6
146	5
133	1 6
120	8
119	16 4
118	100 0
117	6 8
115	5
106	9
105	3 3
104	1 3
103	8
101	3 6
99	5 2
97	6
95	5
94	1 5
93	10 2
92	2 1
91	2 5
90	6
89	6
84	7

Measured Mass	% Int Base
83	6
81	7
79	8
78	8 4
77	79 2
76	2 9
75	1 5
74	1 3
71	9
71	7 1
69	1 5
69	11 2
67	6
66	2 2
65	7 5
64	2 3
63	2 5
62	8
59	6
58	6
57	1 6
56	6
55	1 1
53	6
52	2 9
51	26 5
50	4 6
44	9
43	2 6
42	3 4
41	3 1
40	1 4
39	7 7
38	1 9
37	6
32	9 6
29	8
28	28 9
27	3 1
26	7
18	21 2
17	56 3
17	5 3

E.I. Mass Spectrum of $Me_2Ga[(p\text{-}ClPh)N=C(Me)N(p\text{-}ClPh)]$

Measured Mass	% Int. Base
480	3
479	4
478	7
477	4
476	4
461	4
453	4
452	6
451	3.0
450	1.7
449	10.0
448	2.7
447	13.9
446	1.9
445	7.0
402	3
400	7
399	3
398	1.1
397	4
396	7
395	4
393	6
392	4
390	1.2
388	1.1
386	9
383	1.2
382	4.6
381	6.6
380	33.0
379	15.8
378	72.4
377	12.9
376	7
376	58.3
375	3.0
374	4
369	3
368	2.6
367	14.8
366	18.3
365	83.7
364	44.4
363	100.0
362	35.1
361	95.0
359	9
359	7
357	8
356	6
355	6
354	7
352	1.1
352	8
351	2.8
350	3.0
349	7.0
348	5.4
347	11.9
344	9
346	3.3
345	8.8
344	1.3
343	6
342	1.0
341	9
337	7
335	1.3
333	1.5
331	2.0
330	1.3
329	3.4
328	4.3
327	3.7
326	3.6
325	6
313	7
312	9
311	9
310	5
309	1.7
308	6
307	3.7
306	4
305	8.9
282	4
281	1.1
280	2.0
279	4.8
278	3.3
277	7.3
276	1.1
275	5
264	1.3
263	4
262	1.9
244	7
243	1.3
242	2.2
241	3.4
240	9
239	5
238	9
237	8
236	2.4
235	4
234	2.3
214	4
213	4
212	7
211	1.0
210	7
209	1.0
207	9
206	2.2
205	9
203	1.4
202	9
201	2.6
200	1.0
199	4
197	1.3
196	3
195	1.2
192	3
181	4
180	4
177	4
175	4
167	1.0
166	2.9
165	8
164	7
162	3
160	3
158	4
155	2.2
154	23.3
153	7.2
152	66.6
151	9
142	3
140	1.9
139	1.1
138	1.0
137	7
131	4
129	2
127	1.8
125	1.9
121	1.0
119	1.0
118	8
117	2.1
116	9
114	1.1
113	11.1
112	9.2
111	34.3
110	4.0
104	5
103	5
102	1.0
101	11.2
100	9
99	17.5
98	6
91	7
90	3.7
89	1.2
88	3
87	7
86	1.6
85	1.6
84	2.3
78	4
77	1.7
76	4.9
75	14.5
74	1.2
72	6
71	19.5
69	30.0
65	5
64	1.2
63	3.2
62	7
61	4
51	2.2
50	2.9
42	4
41	4
39	1.4
38	4
27	2
17	1.9

E.I. Mass Spectrum of a Sample of $Me_2Ga[(p\text{-}ClPh)N=C(Me)N(p\text{-}ClPh)]$ After Exposure to Damp Nitrogen.

Measured Mass	% Int. Base
536	.8
534	1.7
532	2.2
530	1.7
518	.9
516	1.1
514	.7
439	.6
437	3.0
435	4.0
433	5.9
431	3.0
423	.6
421	3.0
420	.4
418	8.4
418	.9
416	13.0
415	1.0
413	10.9
413	3.7
404	.7
402	1.4
400	1.3
399	.8
388	.8
386	1.3
384	1.1
365	.6
363	1.3
361	1.0
339	5.6
338	1.4
337	24.3
336	3.9
335	38.2
334	1.9
333	28.2
332	.9
331	2.2
329	1.1
327	.6
325	.6
322	1.3
321	20.9
320	3.3
319	72.3
318	6.3
317	83.7
316	4.8
315	67.3
314	.6
313	4.4
307	.7
305	5.2
303	1.2
303	15.7
302	2.4
301	21.9
300	2.3
299	10.7
298	.9
291	.7
289	4.5
287	8.9
286	.9
285	9.3
283	2.7
274	.9
272	2.1
270	4.2
269	.7
268	2.2
261	.6
259	.8
256	.8
254	.8
242	.7
240	.9
238	.5
228	.9
225	.7
224	.5
223	.9
222	1.9
221	36.9
220	7.4
219	86.6
218	8.9
217	91.0
216	2.9
215	52.8
213	.6
211	.7
209	1.0
207	.8
206	.6
205	26.0
204	4.6
203	84.6
202	8.7
201	92.9
200	5.6
199	80.8
191	1.0
190	1.6
189	7.0
188	4.0
187	14.9
186	4.0
185	13.8
184.9	.8
184	.6
183	2.8
182.9	.9
181	.6
173	2.3
172	17.8
172	1.8
171	38.4
170	3.9
169	25.7
168	2.2
158	2.3
157	.9
154	7.0
155	2.9
155	7.2
153	2.2
153	1.9
152	.6
142	.6
139	1.0
137	.8
129	.7
127	1.1
125	.9
127	2.4
119	.6
118	.8
117	.8
116	.8
115	1.3
114	1.1
113	1.6
111	.7
105	2.6
103	16.7
102	8.9
101	98.3
100	14.6
99	100.0
98	5.6
97	.9
95	5.0
88	1.1
87	11.6
86	16.8
85	7.2
84	25.1
83	2.4
82	1.1
81	.6
71	72.8
70	.5
69	62.7
32	.6
31	.9
30	.6
29	1.8
28	.7
28	2.6
28	2.6
27	4.3
26	2.1
19	18.7
18	.9
18	35.3
17	4.6
17	12.2
2643039	3.2
2643627	2.3
2644735	1.9
2691795	20.4
2744117	3.8
2800473	1.3
2861625	.6

E.I. Mass Spectrum of $Me_2Ga[PhN=C(H)NPh]$

Measured Mass	% Int. Base
379	6
365	3
363	7
361	6
339	3
297	1.5
296	9.0
295	2.7
294	12.6
293	4
291	4
283	6
282	3.6
281	26.2
280	6.5
279	40.1
267	7
266	2.9
265	6.2
264	5.5
263	6.7
262	4
237	4
197	2.8
196	21.5
195	18.8
194	3.7
193	5
188	6
186	9
180	1.0
177	4
169	9
168	1.1
167	2.0
166	5
163	4
161	8
154	6
152	1.4
149	2.0
141	4
140	7
139	4
137	1.2
136	8
135	7
133	5
132	5
131	4
129	5
125	5
123	1.2
122	3
121	1.1
121	8
120	4
119	2.5
119	6
118	1.3
117	9
115	7
113	3
111	7
111	5
110	5
109	1.2
107	1.0
106	2.7
105	1.8
104	15.2
103	5.5
102	1.1
101	11.5
100	7
99	19.3
98	2.1
98	7
97	2.5
96	1.1
96	3
95	2.1
94	7.9
93	100.0
92	10.8
91	5.7
90	7
89	1.4
88	6
87	2.6
86	2.0
85	1.5
85	3.0
84	1.3
84	2.8
83	2.3
82	1.8
81	6.0
80	6
79	1.4
78	6.4
77	59.6
76	3.7
75	2.4
74	1.8
73	8
72	8
71	3.1
71	26.2
70	2.5
69	13.4
69	38.2
68	2.4
67	3.7
66	10.5
65	13.6
64	3.6
63	4.2
62	1.2
61	4
60	8
59	18.7
58	6.2
57	6.7
56	1.8
55	5.8
54	1.6
53	1.7
52	5.0
51	29.3
50	7.5
49	7
45	4.6
44	1.8
44	1.2
43	7.3
43	6.9
42	2.2
41	10.3
40	2.5
40	1.0
39	13.8
38	3.3
37	1.2

E.I. Mass Spectrum of $Me_2Ga[(p\text{-}MePh)N=C(Ph)N(p\text{-}MePh)]$

Measured Mass	% Int. Base
402	.6
401	5.1
400	17.9
399	8.6
398	25.6
397	2.2
387	1.6
386	12.1
385	51.3
384	19.0
383	69.2
371	1.3
370	2.3
369	5.0
368	1.5
367	4.1
302	1.3
301	10.8
300	39.6
299	15.6
298	2.0
297	2.1
296	.4
295	1.2
284	.8
283	1.1
282	.4
271	.5
268	.5
267	1.2
266	.5
265	1.8
221	.6
209	1.2
208	1.0
207	1.0
202	2.4
197	1.6
196	5.3
195	32.1
194	100.0
193	3.9
192	1.9
191	.7
190	.8
189	.6
182	.7
181	4.5
180	4.0
179	2.4
178	1.3
177	1.7
176	.4
168	.4
167	2.1
166	1.2
165	2.3
164	1.4
163	16.1
162	2.1
161	24.9
154	.5
153	.8
152	1.8
151	.8
150	1.4
149	3.9
148	1.0
142	1.0
141	1.6
140	.7
139	.5
136	.8
135	1.2
134	.4
131	.6
128	.8
127	.4
118	.9
116	1.4
115	.7
107	.5
106	3.0
105	1.1
104	3.9
103	1.9
102	.7
101	8.2
100	.5
99	12.1
95	.6
92	8.9
91	80.7
90	6.8
89	10.6
87	.5
86	.9
85	.4
84	1.3
83	.4
81	.4
80	.7
79	4.5
78	6.0
77	20.9
76	2.8
75	1.1
74	.6
71	.5
71	10.0
69	.7
69	19.9
67	.4
67	.4
66	4.0
65	40.4
64	2.9
63	7.1
62	.9
57	1.1
55	.6
54	.8
53	2.7
52	3.7
51	10.1
50	2.8
43	.8
41	6.6
40	1.0
39	10.3
38	.6
29	.8
28	.7
27	1.4
18	1.8

E.I. Mass Spectrum of $Me_2Ga[(p\text{-}MePh)N=C(Me)N(p\text{-}MePh)]$

Measured Mass	% Int. Base	Mass	% Int. Base
339.1240	2.5	89.0050	3.4
338.1247	11.8	83.9140	.7
337.1244	4.6	80.0163	1.7
336.1224	17.0	78.0048	1.9
335.1181	1.7	77.0025	3.7
325.1344	1.3	75.9930	.6
324.0962	13.4	70.8908	5.2
323.0925	68.7	68.8936	8.1
322.0943	20.0	66.0083	1.0
321.0912	98.9	65.0047	15.0
308.8567	3.1	63.9928	1.1
307.0147	6.9	62.9885	2.6
306.0619	1.8	53.0049	.7
305.0538	8.3	51.9992	.9
291.9665	1.4	50.9925	1.9
267.0535	2.1	49.9816	.7
266.0326	.6	42.0033	.6
265.0325	3.1	41.0048	14
259.1451	3.7	39.9945	2.9
238.1399	19.5	27.9833	1.0
237.1213	11.8	26.9963	.5
236.2070	1.9	17.9989	.5
235.1116	.8		
222.1034	1.4		
221.0885	1.9		
214.0072	.8		
213.9987	1.0		
194.0804	.7		
188.9848	.6		
181.0647	1.7		
180.0555	2.0		
176.9767	.7		
174.9698	1.1		
145.0445	.7		
133.0537	10.8		
132.0529	100.0		
131.0417	2.4		
119.0479	.4		
118.0366	3.7		
117.0297	.8		
116.0223	.5		
107.0427	7.2		
106.0336	2.1		
105.0328	.8		
104.0207	.9		
103.0127	.5		
100.9383	3.9		
98.9390	6.1		
92.0248	3.5		
91.0208	44.2		
90.0117	2.7		

E.I. Mass Spectrum of $Me_2Ga[(p\text{-}FPh)N{=}C(Me)N(p\text{-}FPh)]$

Measured Mass	% Int Base
359	7
353	2 0
347	4 7
344	22 6
343	7 7
344	34 4
342	2 4
333	2 2
332	24 1
331	99 9
330	37 4
329	100 0
328	8
327	8
317	4 4
315	11 2
314	3 3
313	12 8
312	9
302	1 7
299	3 2
275	1 6
273	2 5
247	3 6
246	22 9
245	14 9
244	1 3
243	1 2
231	5
230	2 6
226	6 6
228	2 1
224	1 1
220	1 6
219	6
218	2 9
205	1 0
204	2 6
203	7 2
202	1 0
198	3
196	8
195	1 3
194	1 2
193	1 7
183	1 8
184	1 8
181	1 3
179	2 4
158	6
157	7

Measured Mass	% Int Base
151	9
150	1 3
149	1 0
148	1 0
145	6
142	2 4
138	1 0
137	20 7
136	93 9
135	4 1
134	1 1
123	2 4
122	2 4
121	1 3
117	5
112	3 9
111	5 6
110	8 1
109	6 4
108	1 7
107	1 0
105	6
103	1 0
102	9
101	14 7
100	1 2
99	23 1
98	7
97	1 0
96	9 7
95	80 5
94	4 1
93	9
91	6
90	3 1
89	1 2
88	5
87	6
86	2 7
85	8
84	5 6
83	10 9
82	3 8
81	2 4
77	1 1
76	4 0
75	35 8
74	2 9
71	34 6
70	1 2
69	54 9
68	1 8
65	6
64	1 8
63	4 7

Measured Mass	% Int Base
62	1 4
61	5
58	6
57	4 5
56	1 2
55	1 2
54	3 9
53	3 7
52	4
51	2 5
41	9
39	2 6
38	8
31	6
28	1 4
27	8

E.I. Mass Spectrum of $Me_2Ga[C_6H_{11}N=C(NC_4H_8O)NC_6H_{11}]$

Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base
494	.4	312	.5	212	.5	114	2.7
493	.3	311	.4	211	.9	113	14.9
492	1.1	310	.7	210	.5	112	2.1
491	.3	309	1.3	209	3.1	111	.3
490	.8	308	9.2	208	23.0	111	.7
478	.3	307	50.5	207	88.4	110	2.6
476	.3	306	14.0	206	43.9	109	4.3
464	.4	305	68.5	205	17.8	108	.8
463	.5	304	1.4	204	.4	107	1.0
462	1.3	303	.8	201	.5	106	.3
460	1.0	302	.5	199	.6	102	.5
413	.4	301	.3	198	.5	101	19.3
407	.4	300	.3	197	.5	100	3.0
405	1.1	299	.4	196	1.4	100	1.1
403	1.2	298	.5	195	6.6	99	28.1
396	.6	297	.6	194	.6	98	1.7
395	3.2	296	1.4	193	1.6	98	.8
394	47.1	295	1.9	192	1.6	97	4.2
393	29.0	294	8.2	191	10.1	97	1.1
392	95.7	293	4.4	190	.4	96	7.1
391	2.3	292	5.4	189	.6	95	6.3
390	4.1	291	5.4	188	4.0	94	.7
389	.9	290	1.7	187	6.9	93	.4
388	1.6	289	3.6	186	19.0	89	.4
387	.5	288	14.1	185	9.0	88	3.6
386	1.8	287	9.9	184	20.8	87	2.7
384	1.2	286	38.8	183	1.0	87	1.5
381	.4	285	18.8	182	.8	86	9.1
380	2.6	284	29.5	181	.8	86	1.1
379	19.8	283	12.0	180	1.0	85	2.8
378	85.8	280	.5	179	3.2	84	3.3
377	29.8	279	.5	178	8.6	84	1.7
376	100.0	278	2.3	177	20.8	83	39.3
375	1.5	277	11.6	176	.6	82	13.2
374	3.7	276	2.8	175	.5	81	24.5
373	1.8	275	17.0	173	.5	80	1.1
372	6.4	274	3.0	172	7.5	79	2.1
371	1.2	273	1.5	171	1.4	78	.4
370	4.7	272	9.0	170	11.6	77	1.0
369	.4	271	1.1	169	.6	76	.3
364	.9	270	8.4	168	1.3	75	.6
363	.6	269	.6	167	.5	71	.3
362	1.9	268	2.0	166	1.4	71	4.6
361	.6	264	.5	165	8.6	70	1.1
360	2.8	263	1.1	164	30.9	69	4.4
359	10.6	262	1.6	163	52.5	68	7.2
358	4.2	261	5.0	162	.3	68	3.2
357	30.3	259	.4	158	.6	67	7.4
356	3.3	258	1.4	157	2.0	66	.6
355	22.7	257	1.6	156	1.7	65	.7
350	.6	256	3.2	155	2.7	58	1.1
349	1.2	255	2.3	154	1.7	57	2.8
348	5.8	254	2.1	153	1.5	56	7.9
347	1.8	253	.3	152	7.1	55	32.9
346	7.8	251	.6	151	10.4	54	4.3
345	.5	250	.8	150	3.7	53	4.3
344	.7	249	.8	149	4.5	52	.8
343	.9	248	.9	144	.4	51	.7
342	.7	247	.7	143	1.8	44	.6
341	.8	246	.3	142	7.7	43	13.6
334	.5	245	1.8	141	3.0	42	2.9
332	.3	243	.9	140	11.4	41	17.1
331	.4	242	.5	139	.7	40	.8
330	.9	240	.6	138	1.6	39	5.9
329	1.2	236	.3	137	2.3		
328	.8	228	.7	136	1.8		
327	2.5	227	.5	135	.7		
326	.4	226	1.3	129	1.2		
325	1.7	225	2.8	128	.4		
323	.6	224	.9	127	2.7		
322	.4	223	4.6	126	4.1		
321	.7	222	1.6	125	41.0		
320	1.7	221	.9	124	20.5		
319	.7	220	.5	123	13.1		
318	1.7	217	.4	122	.7		
317	.4	216	1.2	121	.9		
316	.6	215	.6	119	.4		
313	.3	214	.7	115	.4		
		213	.5				

E.I. Mass Spectrum of

$Me_2Ga[C_6H_{11}N=C(Me)NC_6H_{11}]$

Measured Mass	% Int. Base	Measured Mass	% Int. Base
367	.6	126	1.3
323	.7	125	2.2
322	2.1	124	6.1
321	1.7	123	.8
320	2.9	122	1.6
319	.8	112	.5
309	1.1	112	.6
308	12.4	111	1.2
307	69.6	111	.6
306	19.0	110	.7
305	100.0	110	.5
304	.4	109	.5
303	1.0	104	.4
291	1.1	101	7.2
289	1.0	100	.7
279	.4	99	1.3
277	.8	99	10.7
267	.5	98	10.2
261	1.7	98	.6
249	2.3	97	1.0
247	.7	96	.9
237	.5	94	.4
235	.4	87	.6
223	2.6	86	.5
222	11.0	86	.7
221	1.6	85	.8
207	.8	85	1.1
196	.4	84	1.2
195	.6	84	1.1
184	2.1	83	4.4
182	1.7	82	2.8
181	.8	81	5.5
180	1.8	80	.4
179	4.1	79	1.1
168	.7	77	.6
167	.8	72	.7
166	1.0	71	3.2
165	1.4	70	1.0
154	.8	69	1.0
153	.5	69	1.0
152	.7	68	4.1
151	1.1	67	2.0
142	.5	65	.4
141	5.8	60	.8
141	.5	59	17.5
140	5.9	58	.8
140	.6	57	.5
139	4.5	56	3.4
138	.5	55	10.4
131	.4	54	1.7
129	.8	53	1.9
		44	1.0
		43	5.2
		42	10.9
		41	11.8
		40	.4
		39	2.3

C.I. Mass Spectrum of

$Me_2Ga[C_6H_{11}N=C(Me)NC_6H_{11}]$

Measured Mass	% Int. Base	Measured Mass	% Int. Base
531	1.1	83	6.1
530	4.2	82	.7
529	17.7	81	1.1
528	9.4	71	.7
527	24.4	69	1.1
393	.6	68	1.2
391	1.0	59	9.3
389	1.5	58	.4
325	1.7	56	1.5
324	10.9	55	3.0
323	39.7	42	.7
322	18.3	41	2.1
321	41.5		
320	2.8		
319	1.1		
309	1.2		
308	9.9		
307	52.1		
306	15.2		
305	79.2		
295	.8		
291	1.7		
289	1.3		
277	.6		
251	.5		
249	.5		
247	.6		
235	.4		
224	3.6		
223	20.2		
222	4.5		
221	1.7		
196	.8		
184	1.6		
182	1.7		
180	.7		
179	1.4		
168	.4		
141	2.5		
140	4.3		
139	.7		
125	1.5		
124	9.9		
122	.8		
101	1.4		
99	.4		
99	2.1		
98	2.9		
97	.5		
96	.5		
84	.4		

E.I. Mass Spectrum of

$Me_2Ga[HN=C(Ph)NH]$

Measured Mass	% Int. Base
528.4087	.7
527.4040	2.8
526.3933	1.9
525.3940	8.2
524.3989	2.5
523.4005	11.5
522.4019	1.1
521.3875	5.6
495.2816	.6
493.2749	.8
426.3570	.8
425.2511	3.6
424.3597	2.2
423.3589	9.9
422.3609	1.9
421.3576	7.5
409.3074	1.1
407.3013	1.5
405.2865	.6
335.2727	.7
333.2716	.7
325.2578	.9
324.2481	1.3
323.2492	19.0
322.2513	7.8
321.2412	29.7
320.2472	5.0
319.2392	18.2
318.2478	2.2
308.2420	.8
307.2122	4.7
306.2187	3.5
305.1952	12.7
304.2099	5.4
303.2044	11.2
302.2117	3.7
301.2112	2.2
289.1928	.8
287.1689	.8
275.1426	1.2
273.1485	1.1
271.1408	.5
225.1497	.5
219.2215	1.2
218.1629	.7
217.2229	.9
207.1941	.5
206.2007	6.5
205.1986	65.7
204.1962	11.7
203.1973	100.0
202.1367	2.6
201.1162	1.5
200.1126	2.6
199.1071	1.0
198.1151	1.5
189.1683	.8
188.1544	1.1
187.1294	.8
186.1113	3.0
185.0733	.7
184.0784	2.6
182.0864	1.4
174.1276	.6
173.0626	.7
172.0880	1.2
171.0435	1.4
170.0430	1.2
169.0369	1.1
168.0453	.8
164.1550	1.1
163.1471	33.6
162.1507	1.6
161.1484	19.6
153.1340	1.0
152.1368	.7
148.1093	.6
146.1132	1.0
136.0848	.5
123.0491	.5
121.2021	2.9
121.0466	2.5
120.1979	25.0
119.0811	3.5
115.0711	.5
111.0675	.5
105.1671	2.6
104.1611	30.9
103.1554	16.5
103.0592	1.2
102.6200	.7
102.0905	2.9
101.6181	1.0
101.0784	10.4
100.0730	2.4
99.0790	14.3
93.1600	.9
92.1511	.8
91.0436	1.4
89.0452	.6
81.0412	1.8
79.1384	3.0
77.1263	12.0
76.0161	5.6
75.0293	1.8
74.0373	1.7
71.0068	7.0
69.0045	10.7
65.1073	1.0
63.0509	.5
52.0893	1.7
51.0861	5.7
50.0745	3.3
43.0324	2.9
39.0705	1.7
38.0621	.6
28.0502	.8
27.0565	.7

C.I. Mass Spectrum of

$Me_2Ga[HN=C(Ph)NH]$

Measured Mass	% Int. Base
545.2238	.6
543.2357	.6
542.2561	.9
541.2652	3.8
540.2934	1.3
539.2993	4.8
538.3367	.7
537.3134	2.6
529.3256	1.3
528.2783	2.6
527.2902	11.8
526.2834	9.0
525.2848	39.4
524.2891	12.5
523.2875	55.9
522.2840	6.6
521.2746	28.1
507.2133	.7
505.1874	.6
495.2094	1.3
493.1713	2.1
491.1837	1.0
442.3029	.6
441.2910	2.9
440.3182	1.9
439.3117	9.0
438.3113	3.0
437.3126	3.9
428.2440	.5
427.2836	3.9
426.2673	9.2
425.2743	22.7
424.2807	9.2
423.2795	40.5
422.2681	7.1
421.2763	25.0
420.1854	1.2
418.1897	.6
409.2486	1.4
407.2377	1.8
405.2035	.8
341.3066	.9
340.2082	.7
339.3023	1.4
335.2257	.5
325.2574	1.7
324.2271	.8
323.2256	4.8
322.1962	3.1
321.1915	4.6
320.1984	7.5
319.1918	4.5
318.1948	5.6
317.2038	1.6
307.1681	3.7
306.1685	3.3
305.1489	9.1
304.1569	6.6
303.1532	9.0
302.1598	4.8
301.1578	2.4
291.1462	.9
290.1394	.8
289.1429	2.7
287.1409	2.0
275.1138	.6
273.1127	.6
225.1986	.9
222.2046	7.8
221.2028	32.4
220.2001	11.7
219.2007	48.7
217.1553	1.0
206.1685	4.5
205.1640	49.4
204.1641	7.9
203.1617	72.9
202.1091	1.3
200.0881	1.3
198.0795	.8
191.1406	1.1
189.1408	1.4
188.1120	.6
186.1056	.6
184.0547	.5
172.1026	.6
163.1174	6.4
162.1269	1.0
161.1189	9.9
138.0632	.5
122.1913	2.4
121.1856	29.7
121.0237	1.1
120.1769	14.9
119.0247	.9
118.1123	.8
116.1026	.9
104.1475	5.0
103.1381	6.9
102.0667	1.5
101.0667	7.2
100.0635	2.6
99.0699	10.2
94.1584	.7
93.1513	.8
88.0389	.9
86.0384	1.7
78.1213	4.2
77.1198	3.2
76.1081	1.4
70.9980	5.0
68.9973	7.4
51.0793	.8
50.0689	.8
18.0586	100.0
17.0417	15.8

C.I. Mass Spectrum of $Me_2Ga[(o\text{-}MePh)N=C(Me)N(o\text{-}MePh)]$

Measured Mass	% Int. Base
455.1364	.1
398.2478	.2
357.2246	1.0
356.1876	.2
340.1484	.1
339.1185	.7
338.1279	.3
337.1222	.7
323.0780	.6
322.1129	.1
321.0947	.9
241.1453	.2
240.1582	1.4
239.1564	8.0
238.1475	1.4
237.1757	.6
224.1933	.6
223.1840	3.1
222.1436	1.5
178.1329	.1
141.1256	.3
140.1263	.4
134.0876	.2
133.0732	1.0
132.0703	9.8
131.0679	.3
130.0650	.2
125.1037	.1
124.1058	.5
121.0619	.1
120.0676	.3
118.0422	.1
117.0408	.1
108.0701	.4
107.0595	.9
106.0621	.3
105.0508	.1
104.0414	.1
103.0494	.2
102.1171	.3
100.9944	.2
98.9824	.1
98.0679	.2
93.0458	.2
92.0626	.1
91.0385	2.2
89.0247	.3
83.0584	.2
82.0822	.2
78.0321	.1
77.0200	.2

Measured Mass	% Int. Base
68.9920	.1
67.0365	.1
65.0269	1.0
61.0241	.1
60.0376	.1
59.0456	.9
58.0468	.1
56.0376	.1
55.0422	.1
43.0368	.1
42.0289	.1
41.0261	.2
39.0100	.3

E.I. Mass Spectrum of $Me_2Ga[(o\text{-}MePh)N=C(H)N(o\text{-}MePh)]$

Measured Mass	% Int. Nref	Measured Mass	% Int. Nref	Measured Mass	% Int. Nref	Measured Mass	% Int. Nref
431	.2	206	.5	120	1.2	71	5.8
430	.4	205	.3	119	2.6	70	1.1
429	.8	204	.3	118	18.2	69	1.4
417	.3	197	.4	117	4.0	69	.6
416	.3	194	.3	116	.6	69	8.5
415	.6	193	.5	115	.3	68	.7
413	.3	192	.5	115	.2	67	1.7
411	.2	191	.3	113	.8	66	.7
401	.4	191	.9	112	1.0	65	7.1
399	.3	183	.2	111	1.2	64	.8
357	.5	182	.4	111	6.0	63	2.0
356	.5	181	.4	110	1.0	62	.5
355	1.6	180	.6	109	2.0	59	.5
343	.4	179	.4	108	6.8	58	.3
342	.5	178	.4	107	81.9	57	8.4
341	1.2	177	.3	106	21.2	56	1.8
327	.6	177	.4	105	.5	55	3.5
325	.3	175	.2	105	2.4	54	.7
324	.7	168	.3	104	1.5	53	1.0
323	.5	167	.6	103	1.7	52	1.1
322	.9	166	.2	102	.5	51	2.6
310	.6	165	.8	101	24.4	50	.9
309	2.0	164	.3	100	1.3	45	.3
308	.5	163	.6	99	1.1	43	4.3
307	2.9	163	.2	99	28.5	42	.6
295	.2	161	.2	98	.8	41	3.5
284	.4	155	.3	98	.5	40	.3
283	.6	155	.2	97	3.6	40	.3
282	1.0	153	.5	96	1.9	39	3.0
281	4.6	152	.5	95	2.4		
267	.8	151	.7	93	.5		
265	.4	149	1.1	92	1.8		
264	.2	148	.3	91	16.9		
257	.2	147	1.5	90	2.0		
251	.2	145	.3	89	2.9		
249	.3	141	.6	87	.8		
239	.2	140	.2	86	.3		
237	.2	139	.7	86	2.2		
236	.4	138	.5	85	2.5		
226	.2	137	1.0	85	.5		
225	2.7	136	.5	84	1.0		
224	15.4	135	.6	84	3.3		
223	4.2	134	.3	83	3.6		
222	.8	133	1.8	82	.4		
221	1.3	132	1.0	82	1.4		
219	.3	131	1.1	81	3.0		
211	.2	130	.2	80	1.2		
210	1.1	129	.2	79	3.3		
209	5.7	127	.7	78	1.6		
208	2.3	126	.4	77	4.1		
207	8.3	125	1.3	76	.9		
		124	1.0	75	.6		
		123	1.4	74	.5		
		122	.3	73	2.6		
		121	1.4	71	4.0		

E.I. Mass Spectrum of $Me_2Ga[(p\text{-}(i\text{-}Pr)Ph)N{=}C(Ph)N(p\text{-}(i\text{-}Pr)Ph)]$

Measured Mass	% Int. Base
457	1.7
456	4.5
455	2.1
454	6.7
453	.8
443	.7
442	4.6
441	17.6
440	7.7
439	24.9
425	.9
423	1.3
357	2.6
356	9.7
355	1.8
339	.7
338	.5
336	.4
323	1.9
322	.6
321	2.2
314	.9
313	3.8
307	1.1
306	.8
303	1.2
298	.5
297	1.6
238	1.0
224	1.9
223	17.4
222	100.0
221	.9
220	1.0
208	.6
207	2.1
206	2.3
205	.9
181	.5
180	2.2
179	1.8
168	.4
167	.4
163	5.4
162	.7
161	5.1
152	.5
151	.6
149	1.0
141	2.3
140	2.3

Measured Mass	% Int. Base
139	1.0
137	.5
133	.4
132	4.5
125	.6
124	.8
121	.6
120	.8
119	1.0
118	1.1
117	1.7
116	.7
115	1.5
111	.8
109	.4
107	.8
106	.4
105	1.4
104	11.4
103	7.0
102	.9
101	2.3
99	.6
99	3.7
98	3.3
97	1.1
96	.5
95	.5
93	1.6
92	2.1
91	13.8
90	.5
89	.8
85	1.1
84	.6
83	5.5
82	1.2
81	2.1
80	.5
79	2.1
78	4.0
77	7.9
76	1.3
75	.5
71	1.6
71	1.7
70	1.0
69	2.9
69	2.7
68	1.0
67	1.0
65	2.3
63	.6
60	.5
59	9.0

Measured Mass	% Int. Base
57	2.6
56	3.3
55	3.9
54	.9
53	1.4
52	.5
51	1.6
50	.6
44	.5
43	5.8
42	4.0
41	8.7
39	1.9

E.I. Mass Spectrum of $MeGa[(p\text{-}ClPh)N=C(Me)N(p\text{-}ClPh)]_2$

Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base	Smoothed Mass	% Int. Base
629	.1	205	.2	119	.4	74	3.4
627	.2	203	.5	119	1.0	73	2.8
625	.2	202	.4	118	1.0	72	.3
623	.2	201	1.0	117	2.1	71	1.2
402	.2	200	.4	116	.6	70	.6
401	.2	192	.3	114	.9	69	1.7
400	.7	191	.5	113	.2	68	16.5
399	.3	177	.2	113	.1	67	.3
398	1.2	173	.1	113	10.6	66	1.0
397	.3	167	.6	112	.2	65	2.4
396	.7	166	.8	112	2.6	64	1.7
395	.1	165	.2	111	33.2	63	.4
385	.3	164	.5	110	.1	62	1.5
383	.4	163	.2	110	.5	61	2.9
381	.5	163	.1	109	.7	60	5.6
378	.1	162	.4	109	.1	59	1.7
365	.3	161	.1	108	.2	58	.9
364	.2	160	.1	107	.9	57	.4
363	.7	160	.6	106	.3	56	3.7
362	.2	158	.5	105	.5	55	12.2
361	.5	156	.1	104	.8	54	[illegible]
359	.4	155	2.9	103	1.8	53	[illegible]
357	.5	154	.1	102	.9	52	[illegible]
355	.3	154	32.7	101	1.8	51	[illegible]
341	.2	153	10.3	100	.5	50	[illegible]
283	.3	152	.1	99	.2	49	[illegible]
282	1.0	152	100.0	99	4.3	48	[illegible]
281	1.2	151	.2	98	.2	47	[illegible]
280	5.5	151	.1	98	.3	46	[illegible]
279	2.9	151	1.8	97	1.0	45	[illegible]
278	.1	150	.3	97	.3	44	[illegible]
278	8.5	149	2.5	96	.4	43	6.1
277	1.9	140	.6	95	1.8	42	6.5
276	.5	139	.8	94	.4	41	8.1
275	.2	138	.2	93	1.8	40	1.1
264	.1	138	.6	92	.5	39	.5
263	.1	137	1.7	91	2.2	38	4.0
256	.1	137	.4	90	2.3	37	1.6
244	.2	136	1.1	89	.8	36	.9
243	.2	135	.5	88	.5	35	.3
243	.4	134	.6	87	.9	34	.2
242	.5	133	.2	86	.3	33	2.3
241	.4	131	.6	85	1.0	32	.1
240	.3	129	1.6	85	2.2	31	.9
239	.1	128	.5	84	.4	30	.2
237	.3	127	4.8	84	.4	29	4.8
236	.1	126	.1	83	1.2	28	.8
218	.2	126	1.1	82	.9	27	
207	.2	125	.9	81	6.0		
206	.4	123	1.1	80	.8		
205	.1	123	.2	79	.7		
		122	.2	78	.6		
		122	.6	77	3.2		
		121	1.8	76	6.9		
		121	.7	75	24.4		

E.I. Mass Spectrum of MeGa[PhN=C(Ph)NPh][PhN=C(Me)NPh]

Measured Mass	% Int. Nref	Measured Mass	% Int. Nref	Measured Mass	% Int. Nref	Measured Mass	% Int. Nref	Measured Mass	% Int. Nref
561	.2	268	.7	151	2.2	93	1.3	39	6.7
551	.7	267	4.5	150	1.4	92	6.9	38	1.4
550	3.9	266	18.4	149	.6	91	1.8	37	.9
549	11.4	265	9.4	148	.8	90	2.9	32	.3
548	10.3	265	.3	146	.8	89	.3	32	5.5
547	.4	265	1.3	145	.3	88	.7	31	.6
546	42.1	264	1.3	144	.6	86	.6	30	.3
545	.3	263	.6	142	.3	85	.9	29	6.1
545	.5	259	.6	140	.8	85	3.1	29	1.2
544	.6	253	.4	139	.7	83	3.8	28	21.5
541	.2	252	.4	138	1.1	83	4.7	27	5.7
520	.5	252	.6	137	.7	82	3.3	26	1.5
519	.4	244	.4	136	.7	81	4.6	18	1.1
519	.3	243	.3	135	1.7	79	1.4	18	11.5
509	.7	241	1.3	134	2.4	78	1.7		
508	.3	237	.6	134	.5	77	8.6		
507	.3	236	.8	133	.8	76	100.0		
497	.6	235	.3	132	1.2	75	3.5		
486	.3	235	1.5	131	.3	74	1.3		
482	.3	227	.2	130	.9	73	.8		
481	.3	225	1.3	128	1.0	72	.9		
481	2.4	223	2.0	128	1.1	72	.4		
480	1.0	222	.5	127	1.5	71	6.6		
479	3.3	220	1.2	126	1.0	70	1.4		
436	.3	214	.3	125	.9	70	3.0		
420	.6	212	2.2	124	1.5	69	7.7		
420	.3	211	11.1	123	.3	68	.3		
419	.7	210	8.8	122	1.6	68	2.3		
381	.5	210	.3	121	1.3	68	2.1		
368	.5	210	1.3	121	1.4	67	4.2		
364	.6	208	1.0	120	1.6	66	1.5		
363	1.7	208	.7	119	1.0	65	7.2		
362	4.3	207	2.5	118	7.4	63	2.4		
361	.5	198	.4	117	69.1	62	2.0		
353	.4	194	2.4	116	3.2	61	.5		
352	2.5	192	1.2	115	1.9	61	.4		
351	.7	191	2.1	114	1.1	60	.7		
350	3.8	190	.3	112	.9	59	.6		
350	.3	189	.6	111	1.9	58	1.4		
349	.5	189	1.0	110	2.6	57	10.1		
338	.3	188	.3	109	1.8	56	4.2		
336	.7	182	.3	108	2.1	55	9.9		
315	.3	180	.4	107	.7	54	2.6		
313	1.1	178	74.6	106	1.1	53	1.2		
312	.3	177	.4	105	.4	52	2.1		
301	.3	176	.5	104	2.1	51	26.1		
297	.8	165	1.1	103	2.6	50	3.6		
295	.8	164	.2	102	1.6	45	.4		
288	.4	159	.3	101	.5	44	6.0		
275	.3	158	.4	100	.3	43	10.6		
272	.8	157	.5	98	.8	43	3.8		
		156	.5	97	6.1	42	4.3		
		155	.3	96	3.6	41	10.5		
		153	.5	95	2.6	40	1.6		
		152	1.2	94	3.3	39	.8		

E.I. Mass Spectrum of $Cl_2Ga[(p\text{-}ClPh)N=C(Me)N(p\text{-}ClPh)]$

Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base
422	.8	110	1.2	51	4.3
420	2.1	110	.6	50	6.1
419	.4	109	1.5	45	.8
418	5.4	107	1.0	44	2.2
416	1.2	105	.6	43	10.6
379	.5	104	.7	43	2.2
377	.9	103	2.1	42	4.8
282	1.0	102	.6	41	9.6
281	1.3	101	1.8	40	1.1
280	6.1	100	.9	39	4.6
279	3.8	99	5.0	38	1.6
278	9.5	98	2.1	38	1.3
277	3.8	97	3.7	37	.6
244	.8	96	2.2	36	4.1
243	1.6	95	2.4	35	1.1
242	.6	94	.7	32	1.0
237	.9	93	1.0	31	.6
236	1.8	92	.7	29	3.1
201	1.0	91	2.0	29	.7
147	1.0	90	2.4	28	9.1
146	1.2	89	1.3	27	2.5
145	.8	88	.5		
139	.6	87	1.2		
138	3.3	85	2.4		
134	31.8	85	1.6		
133	5.8	84	2.7		
132	100.0	83	5.0		
131	1.9	82	2.0		
149	.6	81	3.7		
140	.7	80	.7		
140	.8	79	1.2		
129	1.0	77	2.5		
128	1.2	76	5.4		
127	.7	75	20.3		
129	2.3	74	2.5		
128	.8	73	1.5		
127	6.0	71	4.5		
126	1.5	70	2.4		
125	2.0	69	7.6		
124	.7	68	1.8		
123	1.0	67	3.2		
122	.8	66	.6		
121	1.4	65	1.5		
119	.5	64	2.1		
118	.7	63	5.0		
117	2.7	62	1.8		
115	.6	61	1.8		
114	1.4	60	1.3		
113	10.5	58	.6		
112	3.3	57	6.6		
111	32.7	56	3.7		
		55	10.0		
		54	1.4		
		53	1.2		
		52	.9		

E.I. Mass Spectrum of H_2tmtaa

Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base
345	3.2	224	1.0	161	.8	116	3.7
344	24.4	223	2.4	160	5.8	115	3.8
343	100.0	222	2.3	159	4.0	115	5.3
343	61.4	222	1.6	159	8.1	114	5.0
342	5.6	221	1.3	158	5.8	114	1.3
330	1.8	220	1.8	158	11.7	113	1.1
329	20.1	220	1.6	157	8.7	113	1.1
328	74.0	219	1.0	157	20.0	111	1.7
328	45.5	219	1.0	156	14.0	110	1.7
327	.5	218	1.9	156	11.3	110	1.6
326	1.5	218	.8	155	8.8	109	1.4
325	.5	216	.7	155	5.1	108	.9
315	.7	215	1.3	154	5.0	108	3.9
315	.6	214	2.7	154	4.0	107	2.6
314	.5	213	1.3	153	2.7	107	2.1
313	.9	213	6.7	153	1.3	106	2.1
312	2.8	212	5.8	152	1.7	106	1.3
312	2.0	212	9.1	152	1.5	105	1.1
311	1.0	211	8.5	151	1.2	105	3.1
311	.5	211	16.6	151	.7	104	2.4
311	.8	210	11.4	151	.6	104	4.6
302	1.4	210	5.0	150	.5	103	3.2
301	2.1	209	2.4	150	1.2	103	5.5
301	1.7	209	2.0	149	2.7	102	4.5
300	.6	208	1.7	148	1.9	102	5.8
298	1.2	207	1.6	147	1.6	101	4.9
289	.5	207	.5	146	4.1	101	.7
288	1.0	207	.5	145	2.9	99	2.8
287	3.4	206	1.1	145	10.4	98	1.6
287	.6	206	.8	144	9.2		
287	1.9	205	1.5	144	8.5	98	1.5
286	5.2	205	1.9	143	5.6	97	1.9
286	1.3	204	1.0	143	8.1	96	1.2
285	2.4	204	.8	142	6.5	96	1.2
285	1.8	204	.6	142	4.7	95	1.1
284	.8	202	.7	141	3.9	94	1.5
273	.6	201	4.0	141	2.4	94	1.0
272	1.8	200	2.3	140	.6	93	2.9
272	1.9	200	7.9	140	1.6	92	3.0
271	3.8	199	29.2	140	2.4	92	17.7
271	1.9	198	16.5	139	2.2	91	14.9
270	1.3	197	58.5	139	2.6	91	12.2
270	.5	196	12.1	138	1.1	90	9.5
262	.9	195	6.4	138	1.1	90	7.4
262	.5	194	2.5	137	1.6	89	5.4
261	1.6	193	1.1	136	.7	89	5.9
261	.6	192	.5	136	1.6	88	5.3
260	2.0	192	1.5	135	.9	88	1.5
260	1.1	188	.8	135	1.5	87	1.3
259	.7	187	.9	134	1.0	87	.5
257	.8	186	3.6	134	4.2	85	2.3
253	.6	185	11.4	133	3.5	84	.7
249	.5	184	9.7	133	35.2	84	.6
248	1.8	184	6.0	132	26.9	83	2.7
247	1.8	183	8.2	132	20.8	82	1.3
247	2.2	182	11.4	131	21.4	82	3.4
246	.6	181	6.7	131	21.2	81	2.6
245	1.8	180	3.7	130	14.6	81	2.1
245	.6	179	1.2	130	14.6	80	2.1
245	.8	178	.9	129	11.1	80	2.7
244	1.1	177	.7	129	7.4	79	1.1
244	.7	175	2.1	128	5.4	79	3.4
242	.6	174	2.2	128	4.0	78	2.0
239	1.1	174	7.8	127	2.4	78	4.4
238	4.6	173	5.7	127	3.2	77	3.6
237	3.3	173	24.6	126	1.8	77	11.8
237	9.1	172	22.0	126	1.2	76	12.0
236	6.8	172	.6	125	1.9	76	6.4
235	2.4	172	32.3	124	.6	75	5.2
235	2.1	171	23.9	124	.9	75	3.0
235	1.6	171	17.0	123	2.8	74	2.2
234	1.1	170	15.4	122	1.0	74	.8
234	1.0	170	9.4	122	.6	73	1.2
233	1.1	169	7.2	121	1.2	72	.6
232	.9	168	5.1	120	.6	72	.7
231	1.0	168	4.1	119	5.1	71	2.2
231	.7	167	2.3	118	2.3	71	1.4
230	1.2	166	1.7	118	5.3	70	1.6
229	.8	166	.5	117	3.6		
225	.7	165	1.3	117	8.4		
		164	1.8	116	7.1		

E.1 Mass Spectrum of $Me_2GaHtmtaa$

Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base
461	1.0	304	.7	211	3.1	149	.6	66	.6
459	2.2	303	1.8	210	1.1	147	.6	65	2.2
458	.8	297	.8	209	1.8	146	1.2	64	.8
448	.7	295	.8	208	.9	145	4.8	63	.7
448	.5	287	.8	207	1.3	144	2.0	57	2.4
446	.6	286	1.0	207	7.3	143	2.7	56	.7
445	1.6	285	.6	206	7.6	142	1.4	55	1.3
443	1.9	281	.6	206	16.8	141	.8	53	.6
442	1.4	279	.5	205	8.4	140	.6	51	.9
441	1.9	273	.6	205	1.7	134	.9	43	2.1
440	.8	272	.8	204	.6	133	8.0	42	1.4
432	.5	271	.6	203	.7	132	2.4	41	2.4
431	4.0	270	.7	202	.6	131	3.2	39	1.5
430	24.7	268	.7	201	3.2	130	3.8	32	.8
429	81.5	265	.5	200	2.2	129	2.0	29	.5
428	42.1	262	.7	199	.8	128	1.6	28	4.6
427	94.3	261	.7	199	4.2	127	1.0	27	.8
426	12.0	260	.6	198	1.2	119	1.5		
425	2.0	259	.5	198	4.0	118	1.7		
418	.8	258	1.3	197	12.5	117	2.2		
415	4.1	257	2.7	196	3.7	116	1.7		
414	31.1	256	1.9	195	3.2	115	2.0		
413	92.7	255	3.7	194	1.3	109	.6		
412	44.7	254	1.1	193	1.0	107	.5		
411	100.0	249	.6	192	1.1	106	.5		
410	2.8	247	.6	191	.8	105	.7		
409	2.8	246	.8	191	1.5	104	.8		
408	.6	245	.9	190	.6	103	1.3		
407	.5	244	.5	190	.9	102	2.0		
406	.6	243	1.7	187	.5	101	2.9		
404	.8	242	1.6	186	1.2	99	2.9		
403	1.0	241	1.9	185	1.6	98	.5		
402	1.1	240	2.4	184	1.9	97	1.3		
401	2.4	239	.8	183	3.5	96	.7		
399	5.7	233	.7	182	3.9	95	.8		
398	7.3	237	2.3	181	.8	93	.6		
397	6.6	236	1.4	180	.7	92	2.9		
396	7.8	235	.7	175	.6	91	1.6		
395	5.0	234	.6	174	.9	90	2.0		
394	2.0	232	.9	177	2.3	89	1.5		
393	.9	231	.9	172	2.7	85	.6		
392	.7	227	.6	171	4.1	83	1.5		
391	.6	226	.7	170	1.7	82	1.3		
388	.5	223	.8	169	2.3	81	1.5		
385	2.6	222	1.2	168	1.7	80	.7		
384	6.7	221	1.0	167	.9	79	.8		
383	4.0	220	.8	160	.6	78	1.0		
381	.6	219	.7	159	1.6	77	3.4		
380	2.4	217	.7	158	2.1	76	1.4		
379	7.1	215	1.1	157	4.7	71	1.8		
357	.7	214	2.1	156	3.1	71	5.6		
		214	2.9	155	1.9	70	.6		
		213	3.1	154	1.4	69	15.1		
		213	4.8	153	.8	68	.8		
		21.	1.4	152	.6	67	1.4		

E.I. Mass Spectrum of MeGatmtaa

Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base
430.6658	.8	197.8816	2.4	131.6880	3.9	90.8165	1.9	44.0116	9.8
429.5939	12.5	197.6771	.6	130.9918	7.1	90.0124	1.9	43.9458	.7
428.6044	36.7	196.9335	11.4	130.8376	.6	89.0122	2.6	43.9025	4.2
427.7122	34.6	195.9589	1.9	130.7150	3.1	87.0218	.9		
426.6729	56.3	195.7498	1.3	129.9957	4.5	85.8895	1.4	43.0530	18.8
425.8103	37.4	194.9317	1.5	129.7440	3.3	85.0659	6.2	42.9634	76.5
425.1252	1.9	193.9450	.7	128.9970	3.4	84.9032	4.6	42.0347	8.0
424.7345	2.2	191.8354	.8	128.7238	2.2	84.0559	4.1	41.9494	6.1
414.4885	.9	191.6319	.7	127.9774	1.3	83.9450	.6	41.0399	19.0
413.5684	14.7	191.3644	1.1	127.7659	.5	82.9035	.5	40.9540	15.6
412.5671	71.2	190.8847	.9	127.7092	.8	83.0556	7.7	40.0358	1.3
411.6614	62.0	190.8572	.7	127.0187	2.2	82.9552	.8	39.0261	6.8
410.5607	100.0	190.1198	.7	126.0678	.9	82.9176	.5	38.9441	5.7
409.7256	47.2	185.8662	1.5	125.0825	1.6	82.8617	2.9	31.0090	3.0
397.7032	.9	184.9309	.7	124.9856	.9	82.0526	5.2	30.9457	2.1
397.4920	1.1	184.6657	.8	124.7557	1.2	81.8508	2.5	30.0250	1.9
397.3086	.6	183.8850	2.2	124.0365	1.1	81.0417	8.9	29.9590	.8
396.5621	3.4	182.9259	1.4	123.0607	1.5	80.8771	3.9		
396.0278	.6	181.9204	1.9	122.9880	1.0	80.8290	1.6		
395.5628	2.0	180.9223	2.6	122.8954	.6	79.8711	.5		
394.9964	1.6	180.6077	.6	122.7760	2.0	79.0296	4.0		
394.5355	1.2	179.9770	.7	121.8132	1.1	78.8581	1.3		
393.6837	.6	173.0007	.7	121.0483	.8	78.0254	.7		
343.7923	2.7	172.9254	.9	119.0187	1.7	77.0170	7.0		
342.8397	2.6	171.9834	2.5	118.7283	1.3	76.9162	1.0		
342.1805	.7			117.9825	.8	76.8790	.8		
329.8936	.6	171.6374	.9	117.8593	.5	76.8526	2.1		
328.7261	2.3	170.9703	3.1	117.7205	1.6	76.0235	2.0		
328.4505	.9	170.7627	1.4	116.9937	3.8	75.8461	1.3		
328.0212	1.7	169.9865	1.1	116.7125	1.1	74.9890	.6		
303.1996	1.8	168.9744	3.8	115.9942	2.5	73.0058	3.0		
302.7777	1.8	168.6332	1.6	115.7520	1.7	72.8629	2.5		
295.7827	.6	167.8692	.7	115.0161	1.2	71.9868	.7		
279.0178	.8	166.8967	.7	114.9613	1.2	71.0710	8.7		
278.7867	1.1	166.8320	.9	114.8209	2.0	71.0092	1.1		
277.8946	.6	165.7273	.5	114.7487	1.6	70.9046	18.3		
277.2710	.8	165.0388	1.2	112.0361	1.6	70.7587	5.8		
276.5995	.7	160.9926	.5	111.0663	4.1	70.0607	5.6		
266.2979	.5	158.9792	.8	110.9653	.8	69.8970	2.5		
260.7423	.6	157.9803	1.2	110.8095	1.7	69.0471	21.7		
256.9707	.7	157.6836	1.0	110.0478	2.1	68.9044	32.3		
256.9159	1.6	156.9879	2.7	109.8077	1.9	68.7627	14.5		
256.0120	1.0	156.6331	1.4	109.0559	3.0	68.0405	9.0		
255.7868	1.3	155.9773	3.6	108.7945	1.5	67.9294	.6		
254.9634	2.0	155.8400	.5	108.0335	1.9	67.8975	1.2		
242.9278	.7	155.6311	2.2	107.0227	3.1	67.0279	6.1		
241.8744	1.2	155.0555	1.5	105.0246	1.2	66.9179	1.0		
240.8860	.5	154.9436	1.0	104.0172	.8	66.8756	3.7		
240.7140	.7	153.6737	.5	103.7803	.7	66.0259	3.2		
229.8287	1.4	151.7202	.9	103.0079	2.0	65.0125	4.9		
228.7208	.6	148.9652	8.6	102.8605	.5	64.8866	1.9		
228.5116	.5	148.7494	1.5	102.7662	1.1	64.8428	1.1		
226.9473	1.6	148.6073	1.9	102.0182	.7	64.0049	1.5		
225.9945	2.0	146.6943	.7	101.9687	1.0	63.8536	.5		
225.7806	.5	145.9848	.6	101.7932	.5	62.9815	.8		
228.9335	1.5	144.9990	4.2	101.7464	1.2	61.0070	6.7		
218.9967	.5	144.0294	1.5	101.0410	1.4	60.8743	5.3		
217.8944	.8	142.8000	.9	100.9789	1.6	60.0082	4.6		
214.3793	2.1	143.6817	1.2	100.8984	1.9	59.8652	3.2		
213.8939	3.4	142.9865	3.1	100.7441	1.2	59.0337	1.7		
213.4299	3.1	142.7258	1.3	100.6621	.5	58.8973	1.6		
212.9104	4.2	142.6762	.9	99.0526	2.8	58.0432	1.6		
212.3641	.7	142.0008	1.1	98.9421	3.0	57.0407	16.9		
211.9019	.6	140.0268	.7	98.8472	1.8	56.9234	10.6		
210.9959	.5	139.9778	.7	98.7368	1.3	56.0457	7.4		
210.4260	.8	139.7158	.9	98.0880	4.5	55.9840	.6		
209.6219	.5	138.0482	2.0	97.8118	1.5	55.9194	5.8		
208.8841	1.1	137.8269	.5	97.0584	7.4	55.0338	18.7		
207.4125	2.2	137.0744	2.0	96.8549	5.1	54.9246	11.3		
206.9024	4.7	136.7703	.8	96.0464	4.9	54.0042	2.0		
206.4176	12.9	136.6747	1.2	95.9587	1.2	53.8993	1.0		
205.8746	11.8	136.0422	1.6	95.0442	6.9	53.0294	2.5		
205.4084	11.2	135.0656	.9	94.8676	1.3	52.9251	2.0		
204.9529	5.9	134.8601	.9	94.0394	1.6	52.0233	2.6		
204.4558	.8	134.0653	.8	93.8464	.6	51.9225	1.0		
200.9540	.5	132.9526	.9	93.0245	6.3	51.0041	1.5		
200.7756	.7	133.0148	8.4	92.8491	2.2	50.9049	1.0		
199.7934	1.0	132.8799	.8	92.0224	4.5	50.0048	2.0		
198.9125	4.5	132.7422	4.4	91.8168	3.6	45.0298	7.7		
198.6374	.6	131.9926	7.4	91.0130	2.6	44.9339	2.1		
198.0301	1.0	131.8263	1.9	90.9416	.7	44.8973	.6		

E.I. Mass Spectrum of $Me_2InI.PPh_3$

Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base
528	.1	260	7.2	151	.1	84	.1
523	.1	259	.3	151	2.8	83	3.1
521	.3	259	1.0	150	.9	82	2.1
520	2.2	258	.4	149	.1	81	5.9
519	10.1	257	.3	147	.1	80	2.3
517	.4	256	36.9	146	2.6	79	1.0
508	.1	255	.7	145	66.6	78	5.4
498	.2	254	2.0	144	1.9	77	13.7
449	.2	252	.1	143	3.8	76	2.7
448	1.1	251	.2	142	1.4	75	2.4
447	3.3	250	.6	141	4.3	74	2.4
446	2.6	246	.1	141	.2	71	.5
445	6.7	245	.1	140	.8	70	.2
443	.2	244	.7	140	.1	69	1.0
421	.1	242	.4	139	4.4	69	1.6
419	.2	241	21.2	139	.2	68	.1
416	.8	239	.8	138	.2	68	.6
409	.8	233	.6	137	.1	67	.3
408	4.4	231	.4	137	.3	66	.2
407	18.6	230	.6	135	.1	65	3.5
406	.2	229	.5	134	.7	64	.6
405	.9	228	.6	133	7.1	63	3.8
395	.2	227	.2	132	.9	62	.7
394	.4	226	.4	131	4.2	61	.1
393	.8	221	.1	130	.1	58	.3
393	.1	220	.4	130	6.2	57	6.2
391	.2	217	.2	129	.1	56	.1
389	.7	216	.2	129	.1	56	1.5
386	2.2	215	.7	129	1.5	55	.5
385	.2	208	.1	128	.4	53	.3
384	.3	207	.4	128	.1	52	2.9
383	.3	204	.1	128	3.7	51	23.6
379	.3	203	.3	128	1.0	50	6.2
378	3.0	202	.4	127	6.4	49	.1
377	15.6	201	.2	126	1.7	45	.2
376	.1	200	.2	125	.3	44	.4
375	.6	197	.2	124	.1	43	.7
371	.4	196	.1	123	.3	41	1.1
370	2.2	196	.2	122	.1	40	.4
369	2.9	196	.2	121	.3		
368	.6	195	.2	120	1.2		
357	.1	195	.3	119	.1		
356	.1	194	.2	119	.1		
343	.4	193	.2	117	.2		
339	.3	191	.1	116	1.2		
327	.1	190	.7	116	.2		
325	.1	190	.4	115	50.6		
323	.5	189	.4	114	.3		
322	1.9	187	.4	113	.7		
320	.2	186	3.9	113	2.2		
319	.6	185	27.8	111	.2		
313	.4	184	.2	110	.2		
301	.3	184	33.9	109	6.0		
295	.2	183	.3	108	59.2		
294	.3	182	87.5	107	33.7		
293	.3	182	5.0	106	.1		
291	.1	181	.6	106	.1		
282	.2	181	4.5	106	.9		
281	.3	180	.2	105	.8		
281	1.0	180	.2	104	.5		
280	1.1	178	.1	103	.5		
279	.2	176	.1	102	1.8		
279	.4	171	.8	101	.5		
279	.2	170	5.3	100	.2		
278	.4	169	.8	99	.3		
278	.3	168	.3	98	.4		
277	.3	166	.1	97	.2		
277	.6	165	.6	96	.2		
276	.4	165	.1	95	.2		
275	.1	164	.2	95	.2		
274	.5	163	.2	94	.2		
274	.2	160	.2	93	.5		
273	2.9	159	1.5	92	1.0		
272	3.5	158	1.2	91	1.7		
267	.3	157	9.9	90	.4		
265	.4	156	.4	89	2.3		
264	7.5	155	1.4	88	.5		
263	.3	154	5.5	87	.7		
263	44.7	153	5.2	86	.3		
262	100.0	152	19.1	85	.1		
261	45.1						

E.I. Mass Spectrum of $Me_2InL[(Ph_2P)_2CH_2]$

Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base
477	.2	477	.1	384	97.2	277	.2	213	.1
459	.1	476	.0	383	11.2	277	.2	213	.1
442	.4	475	1.2	382	.2	276	.0	213	.0
441	1.4	473	.2	382	.4	276	.0	213	.1
439	.1	465	.2	381	.1	275	1.2	213	.4
409	.1	463	.2	381	.2	274	.5	212	.2
407	.2	462	.1	380	.0	273	1.5	212	.2
386	.2	461	.2	380	.0	272	.1	212	.0
385	1.0	453	.1	380	.1	272	.5	212	.1
384	9.3	448	.2	372	.1	271	.2	211	.1
383	20.6	447	.5	371	.1	270	.1	211	.1
382	.3	446	.1	371	.1	265	.3	211	.1
381	.6	443	.1	370	1.0	264	0.0	211	.0
371	.2	442	.2	369	.1	263	.1	211	.2
370	.8	441	.0	368	.1	263	80.4	210	.1
369	1.8	435	.1	365	.1	262	78.5	209	.0
368	.4	429	.1	358	.0	261	12.1	209	.0
367	1.0	427	.1	357	.1	260	1.5	208	.3
355	.0	423	.0	355	.1	260	1.2	208	.1
352	.2	417	.0	353	.1	259	.3	208	.0
351	.4	416	.1	338	.0	259	.1	207	1.3
350	.3	416	.3	336	.1	259	.0	207	.3
349	1.0	415	.0	329	.1	258	.3	206	.1
341	.0	415	.7	327	.1	236	4.0	205	.1
331	.2	413	.2	322	.1	255	.1	205	.0
330	1.2	413	.1	321	.3	255	.1	205	.2
329	3.8	413	.3	320	.3	254	.1	204	.0
328	.0	412	.6	319	.3	249	.1	203	.1
327	.1	411	.9	309	.3	248	.0	202	.3
326	.1	411	.9	308	7.8	245	.2	201	2.0
325	.2	410	.7	307	16.2	243	.2	200	28.9
323	.1	410	.5	306	5.5	242	.1	199	.1
319	.1	409	.5	305	5.5	242	.0	199	90.4
317	.1	408	.2	304	.2	241	2.0	198	.2
313	.1	408	.3	294	.7	241	.1	198	.1
311	.1	407	.1	293	2.0	239	.1	198	4.1
307	.8	407	.1	292	.2	236	.0	197	.1
306	4.1	407	.1	291	.2	253	.0	197	22.3
305	11.6	406	.1	290	.3	231	.1	196	.0
301	.1	406	.1	289	.0	231	.1	196	.0
300	1.1	403	.0	287	.0	230	.0	196	8.0
299	3.5	402	.0	285	.0	229	.0	195	1.2
298	.1	402	.0	284	.1	228	.0	195	5.3
297	.2	402	.1	282	.0	227	.1	194	.0
293	.2	401	1.2	282	.1	226	.1	194	.1
292	.5	400	2.7	282	.0	225	.1	194	2.0
291	1.4	399	.7	282	.1	221	.1	193	.1
281	.0	398	.1	281	1.2	220	.1	193	.1
280	.2	398	1.2	280	.4	216	.2	193	.0
279	.5	397	.0	280	1.4	215	.1	192	.2
278	.1	389	.1	279	.2	215	.5	192	.0
		388	.1	279	.7	214	.1	192	.1
		387	2.0	278	.0	214	.0	191	.1
		386	17.7	278	.2	214	.0	191	.1
		385	78.5	278	.1	214	.3	191	.0

continued overleaf

Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base
190	.2	154	2.6	125	.1	89	4.6	61	.2
189	.2	153	6.8	125	.1	88	.4	59	.1
188	.1	152	.0	125	.0	87	.4	58	.5
188	.1	152	18.9	125	.2	84	.1	57	.4
187	.8	151	3.6	124	.1	84	.1	57	8.3
186	4.1	150	.0	123	1.3	84	.4	56	1.5
185	.1	150	.6	122	24.3	83	.2	55	.4
185	26.7	149	.0	121	100.0	83	4.6	54	.2
184	.0	149	.1	120	.0	82	.1	53	.1
184	.0	147	.5	120	6.8	82	2.5	53	1.6
184	19.1	146	1.1	119	.0	81	.1	52	3.9
183	.2	145	11.4	119	1.5	81	6.3	51	30.5
183	80.7	144	1.0	118	.0	80	.1	50	5.7
182	.8	143	.1	117	.1	80	.0	49	.0
182	2.8	143	.6	116	1.5	80	2.5	49	.1
181	1.4	142	.8	116	.0	79	.0	49	.3
181	4.1	142	.1	115	12.8	79	13.2	48	.0
180	1.2	141	5.0	115	6.3	78	20.3	45	1.5
179	3.8	140	.1	114	.6	77	.1	44	.3
178	1.7	140	.7	113	.2	77	60.9	43	.5
178	1.6	139	.0	113	.5	77	.1	42	.1
177	.5	139	.1	113	.3	76	2.3	41	1.7
177	.0	139	4.6	112	.1	75	2.1	40	.7
177	.1	138	.1	111	.2	74	.0		
177	.0	138	.1	110	.3	74	.2		
177	.1	138	.0	109	5.2	74	.1		
176	.1	138	.1	108	21.5	74	.3		
174	.0	138	.4	107	37.9	74	.1		
173	.1	137	.0	106	.1	74	.3		
172	.6	137	.1	106	.1	74	.1		
171	2.9	137	.1	106	.6	74	.2		
170	7.6	136	.1	106	.0	74	2.2		
169	1.1	135	.1	105	.1	73	1.1		
168	1.6	135	.1	105	.5	73	.3		
167	8.4	134	1.2	104	.4	73	.3		
167	.1	133	10.3	103	1.8	73	.1		
166	.0	132	.6	102	.1	73	.1		
166	12.8	131	.0	102	2.3	73	.2		
165	.1	131	1.4	101	.3	73	.2		
165	.1	130	.1	100	.1	73	.1		
165	.1	130	.1	99	.1	72	.1		
165	24.2	130	.1	99	.1	71	.1		
164	.1	130	.1	99	.1	71	1.4		
164	.1	130	1.9	98	.1	70	.2		
164	1.3	129	1.3	98	.1	70	1.1		
163	.0	129	.2	98	.1	69	.1		
163	.1	128	.2	97	.1	69	.1		
163	.7	128	.3	96	1.8	69	3.7		
162	.1	128	4.4	95	17.7	68	.7		
160	.2	128	.1	94	.0	67	.1		
159	1.6	127	.1	94	.8	66	.8		
158	1.1	127	.3	93	1.0	65	15.4		
157	7.8	127	1.6	92	4.2	64	1.2		
156	.4	127	.9	91	43.0	63	4.7		
155	1.1	126	3.0	90	.8	62	.7		

E.I. Mass Spectrum of $Me_2InI.(Ph_2PCH_2)_2$

Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base
691	.2	386	.2	270	.2	171	2.0	90	.2
657	.1	386	.2	269	.5	170	12.3	89	2.4
656	.6	385	1.0	265	.1	169	1.0	88	.2
655	2.1	385	.3	264	2.5	168	.6	87	.4
608	.1	384	.3	263	21.7	167	1.2	84	.4
606	.1	383	.1	262	75.2	166	1.5	83	6.8
597	.3	380	.2	261	.5	165	4.4	82	2.4
595	.1	373	.3	261	14.3	164	.1	81	5.4
586	.2	372	2.8	260	3.5	164	.3	80	2.4
585	3.0	371	21.3	259	1.0	163	.3	79	2.7
584	13.3	370	66.0	258	.3	160	2.0	78	6.4
583	31.6	369	7.3	256	5.6	159	3.8	77	17.0
582	4.6	368	2.4	254	.3	158	1.3	76	2.0
581	10.8	367	.1	245	.2	157	11.1	75	1.3
563	.2	367	.3	244	.1	156	.4	74	.8
558	.1	365	.1	243	.5	155	.6	71	.2
557	.2	363	.2	241	3.5	154	2.5	71	.1
555	.4	353	.2	241	.2	153	6.3	70	.3
553	.1	351	.2	239	.1	152	29.6	69	.2
545	.3	350	.1	233	.3	151	2.4	69	2.1
544	1.1	348	.1	230	.1	150	.6	68	.4
543	3.8	348	.2	229	.7	147	.2	67	.2
541	.2	346	2.0	228	.4	146	1.8	66	.6
540	.3	345	2.2	227	.2	145	11.4	65	8.9
539	.6	344	3.9	226	.1	144	1.6	64	.5
533	.1	343	3.6	217	.8	143	.8	63	3.2
532	.1	338	.2	216	.6	142	1.6	62	.3
531	.5	337	.2	215	2.7	141	10.4	61	.1
520	.2	333	.2	214	1.1	140	1.2	59	.1
519	.6	325	.4	213	.1	139	7.2	58	.7
515	.2	323	.4	213	5.2	138	.8	57	.4
514	1.2	322	4.0	212	.1	137	.4	57	10.0
513	4.6	321	17.4	212	3.4	136	.6	56	1.5
511	.2	320	1.4	211	.4	135	2.1	55	.4
509	.3	319	2.0	211	.1	134	5.6	53	.4
507	.1	318	.2	211	2.9	133	18.4	52	1.7
506	1.6	317	.1	210	1.0	132	.8	51	13.3
505	.2	311	.1	210	1.1	131	1.2	50	3.2
490	.1	310	.1	209	.3	130	1.2	45	.4
489	.1	310	.2	209	.5	129	1.0	44	.3
481	.1	309	.2	209	.6	128	4.7	43	.6
479	.2	309	.2	208	.1	128	.2	43	.1
478	.2	309	.5	208	.2	127	1.2	2	.2
475	.2	308	.1	208	.1	126	1.0	41	1.5
463	.3	308	.4	207	.2	126	.1	40	.2
462	.1	307	.1	202	.3	126	1.5	39	7.1
456	.2	307	.7	201	.5	125	.1	38	.4
455	.4	306	.1	200	1.1	125	.1		
449	.2	306	.4	199	9.7	125	.1		
447	.3	305	.8	198	.1	124	.2		
446	.2	303	.2	198	1.0	123	.4		
438	.4	302	.4	197	.2	122	2.1		
437	.8	301	1.5	197	.1	121	24.9		
431	.8	300	.1	197	2.3	120	2.0		
430	1.7	295	.8	196	1.8	119	.4		
429	4.6	294	3.0	195	1.6	117	.2		
427	7.5	293	7.0	194	.1	116	2.0		
426	.9	292	.8	194	.1	115	12.9		
426	1.2	291	4.6	194	.9	114	7.2		
425	.7	290	42.0	193	.2	114	.4		
424	.4	289	86.8	192	.9	113	.4		
424	.1	288	.5	191	.3	112	.4		
423	.3	287	.2	190	1.7	111	.2		
423	.3	287	.6	187	1.7	110	1.5		
422	.1	286	.4	186	19.6	109	19.3		
422	.3	286	.1	185	83.5	108	40.0		
421	.1	281	.3	184	.5	107	42.4		
414	.9	280	.2	184	41.9	106	.8		
414	2.8	280	.2	183	100.0	105	.8		
413	.1	279	.2	182	4.9	104	.5		
402	.3	278	.7	181	1.7	103	1.7		
401	1.9	277	4.2	181	7.1	102	2.4		
400	16.1	276	24.4	180	3.0	101	.3		
399	74.9	275	.4	180	.2	99	.1		
398	96.8	275	69.3	180	.7	98	.2		
397	6.7	274	1.9	179	.3	97	.1		
396	.8	273	.9	178	.9	97	.2		
395	1.0	271	.5	177	.3	96	.3		
394	.1	271	.1	173	.2	95	2.7		
394	.2			172	.2	94	.3		
393	.2			172	.1	93	.7		
388	.1			172	.2	92	2.2		
						91	14.2		

E.I. Mass Spectrum of $Me_2InI.AsPh_3$

Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base
692	1.5	268	.4	153	18.4	95	5.2
691	4.9	267	1.0	152	100.0	94	.5
690	30.7	266	.8	151	.8	93	2.5
688	1.2	257	.9	151	.4	91	1.7
598	.5	257	1.0	151	24.1	91	1.5
581	1.1	256	62.5	150	.8	89	2.3
579	13.4	256	.3	149	.7	85	5.0
578	34.9	255	1.3	146	1.6	84	4.9
577	1.8	254	4.4	145	61.4	83	6.5
563	1.0	254	.6	144	.6	82	3.6
536	1.5	252	.7	143	4.1	81	6.5
535	8.0	250	.6	142	.7	80	1.1
534	18.8	246	2.1	142	.5	79	3.5
532	.8	245	3.7	141	3.8	78	9.0
530	.9	244	1.2	140	.4	77	14.2
486	3.9	243	1.2	139	.5	76	.9
467	.5	243	1.5	139	1.4	75	1.5
458	4.1	241	51.0	136	.8	74	3.2
457	15.8	241	1.1	136	.7	73	.8
456	.7	239	1.8	135	.5	72	.6
439	.6	238	.8	131	.5	71	5.0
438	7.5	237	1.1	130	9.2	70	3.9
437	34.3	236	4.3	129	1.6	69	9.9
436	.6	231	.4	128	1.9	69	.7
435	.8	230	7.2	128	.8	68	2.9
385	.8	229	25.4	128	1.5	67	4.3
383	3.4	228	14.5	127	.6	65	.5
383	.6	227	65.1	127	7.6	61	.9
382	.5	226	8.1	126	.9	58	.8
379	1.1	225	1.3	126	.6	57	14.5
374	.4	222	.4	126	2.0	56	3.0
368	8.3	216	.8	125	1.3	55	13.1
366	.3	215	1.6	125	1.4	54	1.1
332	1.0	214	2.6	124	1.8	52	2.5
329	1.3	210	1.1	123	3.3	51	13.7
323	1.3	209	.4	122	.5	50	3.1
322	8.3	207	3.5	119	1.0	44	1.1
321	18.9	206	.8	117	1.4	43	10.7
318	2.7	205	1.1	116	.4	43	1.1
307	7.0	201	1.6	115	77.6	42	2.2
306	37.5	198	.5	113	.5	41	6.2
305	9.0	194	1.5	113	2.0	39	2.7
304	2.8	185	1.0	111	4.6	38	.4
303	7.5	183	.8	110	3.2		
302	.7	183	.3	109	1.7		
301	1.4	179	.9	108	.9		
282	2.8	177	1.8	107	1.5		
281	.6	169	.9	105	1.6		
278	.6	168	.5	102	1.5		
271	6.7	166	1.1	101	.6		
271	.4	165	1.5	101	.5		
		164	.5	99	.7		
		156	.5	98	2.7		
		155	4.9	97	5.5		
		154	20.1	96	4.1		

E.I. Mass Spectrum of $Me_2InI.(Me_2NCH_2)_2$

Measured Mass	% Int. Base
667	.2
556	.2
555	.9
545	.1
543	.1
528	.6
526	.2
525	1.1
515	.1
498	.2
418	.3
417	6.4
414	.6
411	.2
403	.2
400	.4
399	.1
387	.3
386	12.5
385	1.6
383	.2
373	.5
371	.2
368	.3
357	.2
356	.6
341	.2
329	.1
328	.1
309	.2
275	.4
273	.2
272	6.8
270	.3
267	.5
261	35.6
260	.1
259	1.7
258	.8
257	56.8
255	4.7
254	.2
252	.3
242	.9
241	40.2
240	.2
239	2.3
232	2.2
231	23.9
230	.1
229	1.0

Measured Mass	% Int. Base
203	.1
192	.1
191	.2
189	.1
177	.1
175	.1
168	.3
163	.2
161	.1
156	.1
154	.3
151	1.9
150	.2
149	1.0
147	.2
146	6.7
145	88.1
144	2.6
143	14.2
142	.8
141	.2
140	.2
139	.1
138	.2
137	1.0
136	.8
35	.4
133	.1
131	.9
130	16.6
129	1.4
128	2.2
127	10.4
125	.1
124	.1
123	.8
122	.3
120	.1
119	.8
118	.4
117	4.8
116	21.4
115	100.0
113	6.1
111	.2
110	.1
109	.5
105	.2
100	.1
99	1.5
98	.2
97	.5
96	.3
95	1.1
94	.3

Measured Mass	% Int. Base
93	.8
92	.1
85	.5
84	.4
83	1.4
82	.6
81	3.8
80	.2
79	.5
73	.8
72	12.2
71	6.0
70	6.9
69	8.0
68	1.0
67	1.0
66	.1
60	.2
59	14.0
58	97.1
57	7.4
56	10.3
55	2.7
54	1.8
53	.6
52	.2
45	.9
44	6.5
43	8.9
42	40.2
41	5.9
40	1.2
39	.6
31	.2
30	15.4
29	4.7
27	4.0
26	.6

E.I. Mass Spectrum of the Product of the Reaction of Me_4Pb with $GaCl_3$

Measured Mass	% Int. Base
348	2.6
344	1.1
343	1.1
340	.5
335	2.8
334	1.7
333	1.6
320	.5
319	17.9
318	8.1
317	25.8
316	7.5
315	8.4
313	.8
305	.7
304	2.1
303	3.0
302	3.2
301	3.5
300	1.2
299	1.7
298	.6
293	.6
291	.8
289	11.8
288	9.3
287	17.2
286	5.4
285	7.0
283	2.1
281	3.1
279	1.8
276	.5
275	22.2
274	11.2
273	74.9
272	28.5
271	33.6
269	3.3
267	1.5
265	1.0
264	.6
263	.9
261	1.1
260	3.2
259	2.9
258	9.6
257	9.5
256	4.1
255	1.3
254	3.2

Measured Mass	% Int. Base
253	83.0
252	34.2
251	38.4
248	2.8
245	13.3
244	8.9
243	44.2
242	19.2
241	19.8
239	2.4
238	13.2
237	6.8
236	5.9
235	.8
233	.8
231	.6
229	.6
224	.8
223	66.6
222	33.4
221	34.1
220	4.8
219	4.1
218	.7
217	.8
209	3.9
208	48.7
207	30.3
206	29.4
205	.7
203	.6
204	1.7
167	.6
165	2.3
163	2.1
156	1.0
154	.8
153	.6
151	2.4
149	3.0
145	2.7
143	5.5
141	5.0
139	4.1
138	.7
136	3.8
134	5.4
131	7.5
129	12.4
123	.5
123	7.9
122	.6
121	34.7
120	1.2
119	34.0

Measured Mass	% Int. Base
118	.6
117	2.2
116	3.0
108	1.3
107	.5
106	4.4
105	.7
104	4.4
103	2.7
102	1.0
101	39.8
100	1.8
99	57.4
98	1.0
97	.7
93	.6
91	.6
87	1.5
86	4.9
85	.5
85	2.9
84	.5
84	7.7
83	1.0
83	1.0
82	1.0
81	.8
81	.7
75	.7
71	.9
71	22.7
70	.6
69	1.6
69	34.2
67	.5
66	.5
64	1.0
[illegible]	.9
57	1.7
56	.6
55	1.6
53	.8
52	31.7
51	5.2
50	100.0
49	11.2
48	4.1
47	7.0
46	1.6
45	4.6
45	.9
44	1.5
43	4.7
41	2.5

E.I. Mass Spectrum of the Product of the Reaction of Et_4Pb with $GaCl_3$

Measured Mass	% Int. Base
393	1.8
347	2.9
346	1.0
345	3.4
344	1.1
343	.7
341	1.9
335	1.1
334	1.0
317	1.0
303	1.4
302	1.2
301	4.7
300	1.9
299	1.6
295	3.6
294	1.1
293	2.0
289	2.4
288	1.1
287	5.1
286	1.5
285	1.9
279	.7
275	.6
272	.5
271	.6
266	1.1
265	2.0
264	.5
245	.9
245	1.6
244	1.0
243	.7
242	6.1
242	2.9
241	3.1
237	14.1
236	.8
236	5.8
235	6.9
229	.6
225	.5
223	.5
221	.8
220	2.7
219	.8
217	.7
211	.7
209	13.8
208	9.6

Measured Mass	% Int. Base
207	6.9
206	5.9
205	8.6
203	1.3
197.5	.7
196.5	.6
195.5	.5
194.5	.7
191.5	2.2
189.5	1.4
183.5	1.4
182.5	1.4
180.5	.7
179.5	1.2
177.5	2.0
176.5	.8
175.5	1.4
169.5	.5
167	3.6
166.5	.6
165.5	1.4
163	2.0
162	.6
161	2.3
157	1.1
155.5	.6
154	.9
153	1.9
152	1.1
151	3.2
150	2.9
149	22.7
148	.9
147	1.9
145	1.2
141	2.6
140	.9
139	1.9
138	2.5
137	15.6
136	8.0
135	4.7
134	1.7
133	2.1
129	1.0
127	2.9
126	2.0
125	5.8
124	2.5
123	8.0
122	2.5
121	9.9
121	.6
120	1.7
119	4.5

Measured Mass	% Int. Base
117	1.6
115	1.2
113	3.3
112	3.5
111	9.1
110	3.6
109	8.9
108	2.4
107	4.3
106	1.1
105	4.2
104	1.3
99	5.0
99	.7
98	4.0
97	15.9
96	4.2
95	20.0
94	4.4
93	8.9
92	4.1
91	8.3
86	.6
85	13.4
84	4.5
83	16.4
82	12.0
81	51.6
80	3.7
79	5.1
78	1.3
77	4.6
76	.7
73	3.4
72	2.2
71	24.6
70	17.7
69	100.0
69	.6
68	14.1
67	15.2
66	3.4
65	2.1
64	4.9
63	2.0
61	1.2
60	3.9
59	1.7
58	4.0
57	44.7
56	11.6
55	32.1
54	3.5
53	8.6
52	1.1

Measured Mass	% Int. Base
51	2.7
50	1.2
49	.6
46	1.2
45	13.6
44	9.2
43	36.0
43	11.0
42	8.2
41	46.6
40	2.1
40	1.2

E.I. Mass Spectrum of the Product of the Reaction of Me_4Pb with $InCl_3$

Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base
385	.2	241	9.7	146	1.9	83	2.8
380	.2	239	.9	145	74.6	82	1.3
365	1.9	238	14.3	144	.8	81	2.7
344	.7	237	6.4	143	.2	81	.2
363	.8	236	6.6	143	3.9	80	.5
350	.3	234	.2	142	.2	79	1.4
348	.2	233	.3	142	.3	79	.2
347	.4	231	1.1	141	.8	77	1.3
345	.4	229	1.1	139	.3	75	.4
335	2.3	224	.8	138	.3	73	.6
334	1.0	223	58.7	137	.7	72	.4
333	.9	222	28.7	135	.4	71	3.7
319	5.4	221	29.3	134	.3	71	.3
318	2.5	220	4.8	133	.2	70	1.8
317	6.8	219	2.9	131	.3	69	9.6
316	2.0	218	.6	131	.8	69	.5
315	2.9	211	4.3	130	18.6	68	1.0
304	.5	209	8.5	129	1.2	67	2.2
303	.4	208	53.5	128	2.2	66	.3
302	1.0	207	22.3	127	1.5	65	.6
301	.4	206	23.9	126	.6	63	.3
300	.4	205	3.5	124	.3	60	.5
289	3.6	204	1.5	123	.6	59	.4
288	2.1	202	.2	122	.2	58	1.2
287	5.5	200	.2	121	.6	57.5	.4
286	1.7	196	1.9	121	.7	57	7.8
285	1.7	195	.2	120	.3	56	2.4
284	.3	194	2.4	119	.7	55	5.1
275	10.4	191	.2	119	1.6	54	.7
274	5.2	189	.3	116	.5	53	1.0
273	34.8	189	1.6	115	.3	52	.8
272	15.7	187	5.1	115	100.0	51	.6
271	14.0	185	7.4	113	.5	50	2.3
269	.9	183	.5	113	4.3	49	.2
268	.3	182	.4	112	.8	48	.2
264	.6	180	2.1	111	.4	46	.4
260	1.5	177	.2	110	.6	45	1.2
259	1.0	175	.6	109	1.5	44	.6
258	4.9	172	.2	107	.4	44	2.9
257	3.2	168	.2	106	.3	43	6.8
256	2.3	167	.3	105	1.3	43	2.6
254	2.4	167	23.0	101	.9	42	2.2
253	67.1	166	1.0	99	.7	41	5.1
252	30.6	165	73.2	99	1.0	40	.5
251	30.8	164	.8	98	.9	40	.3
250	.5	163	3.4	97	1.9	39	2.1
249	2.1	159	.3	96	.9	39	.2
245	7.9	153	.2	95	2.0	38	1.8
244	3.4	152	.3	94	.7	37	1.0
243	26.7	152	6.7	93	.6		
242	9.6	151	.3	92	.9		
		151	1.2	91	2.0		
		150	21.6	87	.3		
		149	1.2	85	2.2		
		148	.8	84	1.3		

E.1. Mass Spectrum of the Product of the Reaction of Et_4Pb with $InCl_3$

Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base	Measured Mass	% Int. Base
411	.1	233	.2	179	.3	132	1.0	83	6.5
410	.1	231	.3	179	4.6	132	.5	82	3.7
386	.1	229	.4	178	.3	131	.5	81	14.7
385	.1	228	.3	178	.2	130	.2	80	1.4
371	.1	227	.2	177	.5	130	.4	79	2.8
368	.1	225	.3	177	.3	129	1.6	78	1.0
367	.1	225	.8	176	.3	128	.5	77	1.8
366	.1	224	.2	175	.7	128	.1	76	.8
353	.1	223	1.0	174	.3	127	.9	75	1.3
342	.1	222	.2	173	4.0	126	1.0	74	1.8
341	.1	220	.5	172	.1	125	4.5	73	8.4
328	.1	219	.1	171	.7	124	1.1	72	7.9
319	.1	218	.3	169	.4	123	3.1	71	40.0
316	.1	217	.2	168	.4	122	1.3	70	11.4
304	.2	215	.3	167	2.0	121	2.9	69	31.8
295	.2	214	.2	167	.9	121	.2	68	.2
294	.2	213	.5	166	.4	120	.6	68	5.1
293	.4	211	.2	165	3.6	119	1.2	67	5.8
287	.1	211	.4	164	.2	119	.1	66	1.8
280	.2	210	.1	163	.8	118	.3	65	1.2
279	.2	210	.1	163	.1	117	.6	64	3.6
277	.2	209	.6	162	.3	116	.7	63	1.0
275	.2	208	.3	161	.7	115	17.8	62	1.1
273	.2	208	.8	160	.2	114	.4	61	11.7
271	.1	207	.5	160	.1	113	1.6	60	7.6
267	.2	206	.6	159	3.8	113	.7	59	4.3
266	.2	205	1.3	158	.2	112	1.9	58	2.3
265	.8	204	.3	157	.2	111	3.2	57	19.6
264	.2	203	.8	155	.8	110	1.5	56	9.6
263	.2	203	.6	154	.4	109	3.1	55	17.5
261	.2	201	.3	153	.5	108	.9	54	2.4
259	.2	200	.2	153	.1	107	2.6	53	3.2
257	.5	199	.3	152	.6	106	.6	52	.5
256	.5	197	.1	152	.7	105	2.0	51	1.4
255	.3	196	.5	151	.8	104	.9	50	1.1
253	.4	196	.4	151	.7	103	.5	49	1.4
252	.1	195	.2	150	4.4	102	.3	48	.3
250	.2	194	.3	149	16.1	101	.9	47	.8
247	.4	194	.7	148	.5	100	.7	47	1.2
245	.5	193	.4	148	.1	99	2.4	46	16.3
243	.1	192	.5	147	1.0	98	4.3	45	50.4
242	.2	191	.8	146	.5	97	5.1	45	5.1
241	.2	190	.2	145	1.8	96	2.3	44	.5
241	.1	189	.5	144	1.7	95	5.8	44	29.1
239	.2	189	.5	143	.5	94	1.9	43	100.0
238	.1	187	.3	143	.4	93	3.2	42	16.1
237	.7	187	.1	142	.5	92	1.4	41	24.0
236	.7	186	.1	141	.8	91	2.5	41	2.2
235	.2	185	.5	140	.4	90	.8	40	2.1
234	.1	185	.2	139	.7	89	.9	39	9.2
		183	.3	138	1.0	88	2.7	38	1.0
		182	.3	137	4.7	87	1.6	38	1.0
		181	2.4	136	2.8	86	.8	37	.8
		180	.5	135	2.0	85	5.0	37	.2
		180	.2	134	.6	84	2.5		

REFERENCES

REFERENCES

1. C.R.C. Handbook of Chemistry and Physics, 69th Edition (1988-1989) Eds. R.C. Weast, M.J. Astle and W.H. Beyer. C.R.C. Press, Inc., Boca Raton, Florida.
2. G. Wilkinson, F.G.A. Stone, E.W.Abel. (Eds.) Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982.
   a) "Gallium and Indium" by D.G. Tuck, (Vol. 1.)
   b) "Aluminium" by J.J. Eisch, (Vol. 1)
   c) "Non-cyclic Three and Four Co-ordinated Boron Compounds" by J.D. Odom, (Vol. 1.)
   d) "Thallium" by H. Kurosawa, (Vol. 1.)
   e) "Lead" by P.G. Harrison, (Vol. 2.)
3. H. Hoberg and S. Krause. *Angew. Chem. Int. Ed. Engl.*, 1976, **15**, 694.
4. E.O. Fischer and H.P. Hofmann, *Angew. Chem.*, 1957, **69**, 639.
5. K.S. Pitzer and H.S. Gutowsky, *J. Am. Chem. Soc.*, 1946, **68**, 2204.
6. A.W. Laubengayer and W.F. Gilliam, *J. Am. Chem. Soc.*, 1941, **63**, 477.
7. C.H. Hendrickson and D.P. Eyman, *Inorg. Chem.*, 1967, **6**, 1461.
8. E.G. Hoffmann, *Liebigs Ann. Chem.*, 1960, **629**, 104.
9. N. Muller and A.L. Otermat, *Inorg. Chem.*, 1965, **4**, 296.
10. A.W. Laubengayer and G.F. Lengnick, *Inorg. Chem.*, 1966, **5**, 503.
11. H. Schmidbaur, J. Weidleim, H.F. Klein and K. Eiglmeier, *Chem. Ber.*, 1968, **101**, 2268.
12. M.J.S. Gynane and I.J. Worrall, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 547.
13. J.S. Poland and D.G. Tuck, *J. Organomet. Chem.*, 1972, **452**, 315.
14. T.D. Parsons and D.M. Rutter, *J. Am. Chem. Soc.*, 1954, **76**, 1710.
15. G.F. Hennion, P.A. McCusker, E.C. Ashby and A.J. Rutkowski, *J. Am. Chem. Soc.*, 1957, **79**, 5190.
16 P.A. McCusker, G.F. Hennion and E.C. Ashby, *J. Am. Chem. Soc .*, 1957, **79**, 5192.

17. R. Köster and G. Bruno, *Liebigs Ann. Chem.*, 1960, **629**, 89.

18. R. Köster, *Angew. Chem.*, 1961, **73**, 66.

19. R. Köster, G. Benedikt, W. Larbig, K. Reinert and G. Rotermund, *Angew. Chem. Int. Ed. Engl.*, 1964, **3**, 174.

20. J.R. Surtees, *Chem. Ind. (London)*, 1964, 1260.

21. G.E. Coates and R.A. Whitcombe, *J. Chem. Soc.*, 1956, 3351.

22. G.E. Coates, M.L.H. Green and K. Wade, *"Organometallic Compounds"* 3rd edition, Vol. 1. The Main Group Elements by G.E. Coates and K. Wade. Methuen and Co. Ltd., London (1967).

23. N.N. Greenwood, P.G. Perkins and M.E. Twentyman, *J. Chem. Soc., (A)*, 1969, 249.

24. W. Strohmeiner and K. Hümpfner, *Z. Elektrochem.*, 1957, **61**, 1010.

25. F. Heim, A. Schleede and H. Kallmeyer, *Z. Anorg. Allg. Chem.*, 1961, **311**, 260.

26. J.S. Kristoff and D.F. Shriver, *Inorg. Chem.*, 1973, **12**, 1788.

27. L.E. Manzer and G.W. Parshall, *Inorg. Chem.*, 1979, **15**, 3114.

28. L.G. Stevens, B. Park and J.P. Oliver, *J. Inorg. Nucl. Chem.*, 1964, **26**. 97.

29. H. Lehmkuhl, *Angew Chem., 1963*, **75**, 1090.

30. T. Takeshita and W.E. Frankle, *Tetrahedron Lett.*, 1968, 5913.

31. C.A. Smith and M G H Wallbridge, *J. Chem. Soc., (A)*, 1967, 7.

32. F.A. Cotton and J.R. Leto, *J. Chem. Phys.*, 1959, **30**, 993.

33. N.N. Greenwood and T.S. Srivastava, *J. Chem. Soc., (A)*, 1966, 267.

34. N.N. Greenwood and T.S. Srivastava, *J. Chem. Soc., (A)*, 1966, 270.

35. N.N. Greenwood and D.J. Prince, *J. Chem. Soc., (A)*, 1969, 2876.

36. N.R. Davidson and H.C. Brown, *J. Am. Chem. Soc.*, 1942, **64**, 316.

37. G.E. Coates, *J. Chem. Soc.*, 1951, 2003.

38. V.G. Tsvetkov, B.I. Kocyrkin, K.K. Furkin and R.F. Galiullina, *Zn. Obshch. Khim.*, 1977, **47**, 2155.

39. A. Leib, M.T. Emerson and J.P. Oliver, *Inorg. Chem.*, 1965, **4**, 1825.

40. M.J.S. Dewar, D.B. Patterson and W.I. Simpson, *J. Chem. Soc., Dalton Trans.*, 1973, 2381.

41. I.L. Wilson and K. Dehnicke, *J. Organomet. Chem.*, 1974, **67**, 229.

42. J.G. Contreras and D.G. Tuck, *J. Organomet. Chem.*, 1974, **66**, 405.

43. K. Dehnicke and N. Röder, *J. Organomet. Chem.*, 1975, **86**, 335.

44. V.V. Gavrilenko, N.P. Fatyushina, V.A. L'vova, V.S. Kolesov, Y.N. Karaksin and L.I. Zakharkin. *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1973, 126.

45. T. Ehemann and K. Dehnicke, *J. Organomet. Chem.*, 1974, **71**, 191.

46. G.E. Coates and J. Graham, *J. Chem. Soc., 1963*, 233.

47. D. Ulmschneider and J. Goubeau, *Chem. Ber.*, 1957, **90**, 2733.

48. J.R. Johnson, M.G. Van Campen, Jr., and O. Grummitt, *J. Am. Chem. Soc.*, 1938, **60**, 115.

49. H. Meerwein, G. Hinz, H. Majert and H. Sönke, *J. Prakt. Chem.*, 1936, **47**, 251

50. J. Goubeau, R. Epple, D. Ulmschneider and H. Lehmann, *Angew. Chem.*, 1955, **67**, 710.

51. H.C. Brown and K. Murray, *J. Am. Chem. Soc., 1959*, **81**, 4108.

52. D.B. Bigley and D.W. Payling, *J. Inorg. Nucl. Chem.*, 1971, **33**, 1157.

53. H.C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, 1959, **81**, 1512.

54. H.C. Brown and V.H. Dodson, *J. Am. Chem. Soc.*, 1957, **79**, 2302.

55. J.J. Eisch, *J. Am. Chem. Soc.*, 1962, **84**, 3830.

56. A.W. Laubengayer, K. Wade and G. Lengwick, *Inorg. Chem.*, 1962, **1**, 632.

57. L.M. Dennis and W. Patnode, *J. Am. Chem. Soc.*, 1932, **54**, 182

58. C.A. Krause and F.E. Toonder, *Proc. Natl. Acad. Sci (USA)*, 1933, **19**, 292. (Chem. Abstr. 1933, **27**, 2646).

59. H. Gilman and R.G. Jones, *J. Am. Chem. Soc.*, 1940, **62**, 980.

60. L.M. Dennis, R.W. Work, E.G. Rochow and E.M. Chamot, *J. Am. Chem. Soc.*, 1934, **56**, 1047.

61. F. Runge, W. Zimmermann, H. Pfeiffer and I. Pfeiffer, *Z. Anorg. Allg. Chem.*, 1951, **267**, 39.

62. H. Gilman and R.G. Jones, *J. Am. Chem. Soc.*, 1946, **68**, 517.

63. H.P.A. Groll, *J. Am. Chem. Soc.*, 1930, **52**, 2998.

64. F. Challenger and B. Parker, *J. Chem. Soc.*, 1931, 1462.

65. S.F. Birch, *J. Chem. Soc.*, 1934, 1132.

66. A.W. Laubengayer, J.D. Smith and G.G. Ehrlich, *J. Am. Chem. Soc.*, 1961, **83**, 542.

67. G. Mann, A. Haaland and J. Weidlein, *Z. Anorg. Allg. Chem.*, 1973, **398**, 231.

68. G. Mann, H. Olapinski, R. Ott and J. Weidlein, *Z. Anorg. Allg. Chem.*, 1974, **410**, 195.

69. F. Maury and G. Constant, *Polyhedron*, 1984, **3**, 581.

70. I.A. Degnan, unpublished PhD Thesis, University of Warwick, 1989.

71. L. Banford and G.E. Coates, *J. Chem. Soc.*, 1964, 3564.

72. R.S. Tobias, M.J. Sprague and G.E. Glass, *Inorg. Chem.*, 1968, **7**, 1714.

73. H. Olapinski and J. Weidlein, *J. Organomet. Chem., 1973*, **54**, 87.

74. H. Olapinski, J. Weidlein and H.D. Hausen, *J. Organomet. Chem.*, 1974, **64**, 193.

75. G.D. Shier and R.S. Drago, *J. Organomet. Chem.*, 1966, **5**, 330.

76. H.D. Hausen, E. Veigel and H.J. Guder, *Z. Naturforsh., Teil B*, 1974, **29**, 269.

77. T.L. Blundell and H.M. Powell, *Chem. Commun.*, 1967, **54**.

78. E. Frankland, *J. Chem. Soc.*, 1862, **15**, 363.

79. J.R. Johnson and M.G. Van Campen, Jr., *J. Am. Chem. Soc.*, 1938, **60**, 121.

80. C.H. Bamford and D.M. Newitt, *J. Chem. Soc.*, 1946, 695.

81. C.F. Cullis, A. Fish and R.T. Pollard, *Trans. Faraday Soc.*, 1964, **60**, 2224.

82. a) H.C. Brown "Hydroboration" W.A. Benjamin, New York, 1962.
b) *idem* Ch. 4 in "Organometallic Chemistry" Ed. H. Zeiss, Reinhold, New York, 1960.

83. K. Ziegler, Ch. 5 in "Organometallic Chemistry" Ed. H. Zeiss, Reinhold, New York, 1960.

84. R. Köster and P. Binger, "Advances in Inorganic Chemistry and Radiochemistry", 1965, **7**, 263.

85. E.A. Jeffrey and T. Mole, *J. Organomet. Chem.*. 1968, **11**, 393.

86. G.D. Stucky, A.M. McPherson, W.E. Rhine, J.J. Eisch and J.L. Considine, *J. Am. Chem. Soc.*, 1974, **96**, 1941.

87. J. Weidlein, *Z. Anorg. Allg. Chem.*, 1970, **378**, 245.

88. H. Gilman and R.G. Jones, *J. Am. Chem. Soc.*, 1940, **62**, 2353.

89. K. Ziegler, F. Krupp, K. Weyer and W. Larbig, *Liebigs Ann. Chem.*, 1960, **629**, 251.

90. Armour and Co., Ger. Pat., 115,8057 (1963) (Chem. Abstr., 1964, **60**, 10,550)

91. A.T.T. Hsieh, *Inorg. Nucl. Chem. Lett.*, 1970, **6**, 767.

92. T. Mole and J.R. Surtees, *Aust. J. Chem.*, 1964, **17**, 961.

93. J.E. Lloyd and K. Wade, *J. Chem. Soc.*, 1965, 2662.

94. W. Nagata, T. Sugasawa, M. Narisada, T. Wakabayashi and Y. Hayase, *J. Am. Chem. Soc.*, 1967, **89**, 1483.

95. H. Hoberg and I. Tkatchenko, *Liebigs Ann. Chem.*, 1971, **751**, 77.

96. T. Hirabayashi, K. Itoh, S. Sakai and Y. Ishii, *J. Organomet. Chem.*, 1970, **21**, 273.

97. H. Tada, K. Yasuda and R. Okawara, *J. Organomet Chem.*, 1969, **16**, 215.

98. E. Gipstein, P.R. Kippur, M.A. Higgins and B.F. Clark, *J. Org. Chem.*, 1961, **26**, 2947.

99. H. Hoberg, *Leibigs Ann. Chem.*, 1962, **656**, 1.

100. K.D. Fuhrmann and F. Huber, *Z. Naturforsch., Teil B*, 1980, **35**, 1376.

101. A. Ya Yakubovich and N.A. Ginsberg, *Dokl. Akad. Naut. SSSR.*, 1950, **73**, 957. (Chem. Abstr., 1951, **47**, 2857)

102. T. Abe and R. Okawara, *J. Organomet. Chem.*, 1972, **43**, 117.

103. E. Wiberg, T. Johannsen and O. Stecher, *Z. Anorg. Allg. Chem.*, 1943, **251**, 114.

104. J.P. Oliver and L.G. Stevens, *J. Inorg. Nucl. Chem.*, 1962, **24**, 953.

105. W.C. Schumb and H.I. Crane, *J. Am. Chem. Soc.*, 1938, **60**, 306.

106. L.C. Chao and R.D. Riecke. *Synth. React. Inorg. Metal-Org. Chem.*, 1974, **4**, 373.

107. M. Falorni, L. Lardicci and G. Giacomelli, *Tetrahedron Lett.*, 1985, 4949.

108. H. Hartmann and H. Lutsche, *Naturwiss*, 1961, **48**, 601.

109. H. Hartmann and H. Lutsche, *Naturwiss*, 1962, **49**, 182.

110. E. Todt and R. Dötzer, *Z. Anorg. Allg. Chem.*, 1963, **321**, 120.

111. V.A. Fedorov and V.G. Makavenko, *Tr. Khim. Khim. Tekhnol*, 1975, 19. (Chem. Abstr., 1976, **85**, 143,170).

112. H.C. Clark and A.L. Pickard, *J. Organomet. Chem.*, 1967, **8**, 427.

113. J.J. Eisch, *J. Am. Chem. Soc.*, 1962, **84**, 3605.

114. P. Krommes and J.Lorberth, *J. Organomet. Chem.*, 1975, **88**, 329.

115. G.A. Tedorazde, *J. Organomet. Chem.*, 1975, **88**, 1.

116. G.B. Deacon and J.C. Parrot, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 329.

117. G.B. Deacon and J.C. Parrot, *Aust. J. Chem.*, 1971, **24**, 1771.

118. G.B. Deacon and J.C. Parrot, *J. Organomet. Chem.*, 1970, **22**, 287.

119. R.A. Kovar, G. Loaris, H. Derr and J.O. Callaway, *Inorg. Chem.*, 1974, **13**, 1476.

120. R.A. Kovar, H. Derr, D. Brandau and J.O. Callaway, *Inorg. Chem.*, 1975, **14**, 2809.

121. O.T. Beachley, Jr., and R.G. Simmons, *Inorg. Chem.*, 1980, **19**, 1021.

122. S.B. Miller and T.B. Brill, *J. Organomet. Chem.*, 1979, **166**, 293.

123. I.M. Viltorova, N.I. Sheverdina and K.A. Kocheshov, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1967, 2760 (Chem. Abstr. 1968, **69**, 10,497)

124. S.B. Miller, B.L. Jelus and T.B. Brill, *J. Organomet. Chem.*, 1975, **96**, 1.

125. O.T. Beachley, Jr., and R.N. Rusinko, *Inorg. Chem.*, 1979, **18**, 1966.

126. C.A. Kraus and F.E. Toonder, *Proc. Natl. Acad. Sci (U.S.A)*, 1933, **19**, 298.

127. H. Schmidbaur and W. Findeiss, *Angew Chem.*, 1964, **76**, 752.

128. H. Schmidbaur and W. Findeiss, *Angew Chem.*, 1964, **76**, 753.

129. H. Schmidbaur and W. Findeiss, *Chem. Ber.*, 1966, **99**, 2187.

130. H. Schmidbaur and H.F. Klein, *Chem. Ber.*, 1968, **101**, 2278.

131. H. Schmidbaur and H.F. Klein, *Angew Chem. Int. Ed. Engl.* 1966, **5**, 312.

132. H. Schmidbaur and H.F. Klein, *Chem. Ber.*, 1967, **100**, 1129.

133. T. Maeda, H. Tada, K. Yasuda and R. Okawara, *J. Organomet. Chem.*, 1971, **27**, 13.

134. K. Yasuda and R. Okawara, *Inorg. Nucl. Chem. Lett.*, 1967, **3**, 135.

135. M.J.S. Gynane, L.G. Waterworth and I.J. Worrall, *J. Organomet. Chem.*, 1972, **40**, C9.

136. M.J.S. Gynane and I.J. Worrall, *J. Organomet. Chem.*, 1974, **81**, 329.

137. L.C. Chao and R.D. Riecke, *J. Organomet. Chem.*, 1974, **67**, C64.

138. K.J. Klabunde and T.O. Murdock, *J. Org. Chem.*, 1979, **44**, 3901.

139. L.C. Chao and R.D. Riecke, *Synth. React. Inorg. Metal-Org. Chem.*, 1975, **5**, 165.

140. M.J.S. Gynane and I.J. Worrall, *J. Organomet. Chem.*, 1972, **40**, C59.

141. K.B. Starowieski and K.J. Klabunde, *Appl. Organomet. Chem.*, 1989, **3**, 219.

142. M.L.H. Green, P. Mountford, G.J. Smout and S.R. Speel, *Polyhedron*, 1990, **9**, 2763.

143. J.J. Habeeb, F.F. Said and D.G. Tuck, *J. Organomet. Chem.*, 1980, **190**, 325.

144. I.N. Chernykh and A.P. Tomilov, *Elektrokhimiya*, 1974, **10**, 971. (Chem. Abstr., 1974, **81**, 85,209).

145. L.C. Chao and R.D. Riecke, *J. Org. Chem.*, 1975, **40**, 2253.

146. L.M. Golubinskaya, V.I. Bregadze, E.V. Bryuchova, V.I. Svergan, G.K. Semin and O.Y. Okhlobystin, *J. Organomet. Chem.*, 1972, **40**, 275.

147. H. Schumann, U. Hartmann, A. Dietrich and J. Pickardt, *Angew. Chem. Int. Ed. Engl.* 1988, **27**, 1077.

148. H. Schumann, U. Hartmann and W. Wassermann, *Polyhedron*, 1990, **9**, 353.

149. H. Schumann, U. Hartmann, W. Wassermann, O. Just, A. Dietrich, L. Pohl, M. Hostalek and M. Lokai, *Chem. Ber.*, 1991, **124**, 1113.

150. R.S. Steevensz, D.G. Tuck, H.A. Meinema and J.G. Noltes, *Can. J. Chem.*, 1985, **63**, 755.

151. H. Schumann, U. Hartmann, W. Wassermann, A. Dietrich, F.H. Gorlitz, L. Pohl and M. Hostalek, *Chem. Ber.*, 1990, **123**, 2093.

152. A. Boardman, R.W.H. Small and I.J. Worrall, *Inorg. Chim. Acta*, 1986, **119**, L13.

153. D.C. Bradley, H. Chudzynska, M.M. Faktor, D.M. Frigo, M.B. Hursthouse, B. Hussain and L.M. Smith, *Polyhedron*, 1988, **7**, 1289.

154. H.D. Hodes and A.D. Berry, *J. Organomet. Chem.*, 1987, **336**, 299.

155. H. Schmidbaur, H.J. Füller and F.H. Köhler, *J. Organomet. Chem.*, 1975, **99**, 353.

156. H. Schmidbaur and W. Wolfsberger, *Chem. Ber.*, 1967, **100**, 1017.

157. H. Schmidbaur and W. Wolfsberger, *J. Organomet. Chem.*, 1969, **16**, 188.

158. H.C. Clark and A.L. Pickard, *J. Organomet. Chem.*, 1968, **13**, 61.

159. A.T. McPhail, R.W. Miller, C.G. Pitt, G. Gupta and S.C. Srivastava, *J. Chem., Soc., Dalton Trans.*, 1976, 1657.

160. M. Khan, R.C. Steevensz, D.G. Tuck, J.G. Noltes and P.W.R. Corfield, *Inorg. Chem.*, 1980, **19**, 3407.

161. C. Peppe and D.G. Tuck, *Polyhedron*, 1982, **1**, 549.

162. M.A. Khan, C. Peppe and D.G. Tuck, *Organometallics*, 1986, **5**, 525.

163. H. Schmidbaur and O. Glasser, *Angew Chem.*, 1976, **88**, 542.

164. H. Schmidbaur, O. Glasser, C. Krüger and J.C. Sekutowski, *Chem. Ber.*, 1977, **110**, 3517.

165. H. Schmidbaur and H.J. Füller , *Chem. Ber.*, 1977, **110**, 3528.

166. H. Schmidbaur and H.J. Füller , *Chem. Ber.*, 1974, **107**, 3674.

167. K. Mertz, W. Schwarz, B. Eberwein, J. Weidlein, H. Hess and H.D. Hausen, *Z. Anorg. Allg. Chem.*, 1977, **429**, 99.

168. A. Storr and B.S. Thomas, *J. Chem. Soc.(A)*, 1971, 3850.

169. F. Gerstner and J. Weidlein, *Z. Naturforsch., Teil B*, 1978, **33**, 24.

170. H.D. Hausen, F. Gerstner and W. Schwarz, *J. Organomet. Chem.*, 1978, **145**, 277.

171. F. Gerstner, W. Schwarz, H.D. Hausen and J. Weidlein, *J. Organomet. Chem.*, 1979, **175**, 33.

172. G.E. Coates and R.N. Mukherjee, *J. Chem. Soc.*, 1964, 1295.

173. J.T. Leman, A.R. Barron, J.W. Ziller and R.M. Kren, *Polyhedron*, 1989, **8**, 1909.

174. H. Schmidbaur, K. Schwirten and H.H. Pickel, *Chem. Ber.*, 1969, **102**, 564.

175. A. Ardulni and A. Storr, *J. Chem. Soc., Dalton Trans.*, 1974, 503.

176. A.M. Arif, D.C. Bradley, D.M. Frigo, M.B. Hursthouse and B. Hussain. *J. Chem. Soc., Chem. Commun.*, 1985, 783.

177. P. Cocolios, R. Guilard and P. Fournari, *J. Organomet. Chem.*, 1979, **179**, 311.

178. A. Coutsolelos and R. Guilard, *J. Organomet. Chem.*, 1983, **253**, 273.

179. A. Tabard, R. Guilard and K.M. Kadish, *Inorg. Chem.*, 1986, **25**, 4277.

180. C. Lecomte, J. Protas, P. Cocolios and R. Guilard, *Acta. Cryst.*, 1980, **B36**, 2769.

181. D.E. Heaton, R.A. Jones, K.B. Kidd, A.H. Cowley and C.M. Nunn, *Polyhedron*, 1988, **7**, 1901.

182. A.H. Cowley, P.R. Harris, R.A. Jones and C.M. Nunn, *Organometallics*, 1991, **10**, 652.

183. A.H. Cowley, R.A. Jones, M.A. Mardones, J. Ruiz, J.L. Atwood and S.G. Bott, *Angew Chem. Int. Ed. Engl.* 1990, **29**, 1150.

184. M.E. Kenney and A.W. Laubengayer, *J. Am. Chem. Soc.*, 1954, **76**, 4839.

185. G.S. Smith and J.L. Hoard, *J. Am. Chem. Soc.*, 1959, **81**, 3907.

186. G.E. Coates and R.G. Hayter, unpublished results, quoted in ref. 22, pg 347.

187. G.E. Coates and R.G. Hayter, *J. Chem. Soc.*, 1953, 2519.

188. W. Fries, K. Sille, J. Weidlein and A. Haaland, *Spectrochim Acta*, 1980, **36A**, 611.

189. H. Tada, K. Yasuda and R. Okawara, *Inorg. Nucl. Chem. Lett.*, 1967, **3**, 315.

190. I.M. Viktorova, N.I. Sheverdina and K.A. Kocheshkov, *Dokl Akad. Nauk SSSR*, 1971, **198**, 94.

191. M.A. Banks, O.T. Beachley, Jr., H.J. Gysling and H.R. Luss, *Organometallics*, 1990, **9**, 1979.

192. H. Schmidbaur and F. Schindler, *Chem. Ber.*, 1966, **99**, 2178.

193. B. Armer and H. Schmidbaur, *Chem. Ber.*, 1967, **100**, 1521

194. H.D. Hausen, K. Sille, J. Weidlein and W. Schwartz, *J. Organomet. Chem.*, 1978, **160**, 411.

195. J. Weidlein, *Z. Anorg. Allg., Chem.*, 1971, **386**, 129.

196. F.W.B. Einstein, M.M. Gilbert and D.G. Tuck, *J. Chem. Soc., Dalton Trans.*, 1973, 248.

197. J. Habeeb and D.G. Tuck, *Can. J. Chem.*, 1974, **52**, 3950.

198. H.D. Hausen, *J. Organomet. Chem.*, 1972, **39**, C37.

199. H.D. Hausen and H.U. Schwering, *Z. Anorg. Allg. Chem.*, 1973, **398**, 119.

200. H.D. Hausen and H.J. Guder, *J. Organomet. Chem.*, 1973, **57**, 243.

201. I.M. Viktorova, N.I. Sheverdina, A.N. Rodionov and K.A. Kocheshkov, *Dokl. Akad. Nauk. SSSR*, 1969, 315.

202. I.M. Viktorova, N.I. Sheverdina, A.N. Rodionov and K.A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, 1967, **176**, 326.

203. H.D. Hausen, K. Mertz and J. Weidlein, *J. Organomet. Chem.*, 1974, **67**, 7.

204. H.U. Schwering and J. Weidlein, *Chimia*, 1973, **27**, 535.

205. H.U. Schwering and J. Weidlein, *J. Organomet. Chem.*, 1975, **84**, 17.

206. P. Fischer, R. Gräf, J.J. Stezowski and J. Weidlein, *J. Am. Chem. Soc.*, 1977, **99**, 6131.

207. R. Lechler, H.D. Hausen and J. Weidlein, *J. Organomet. Chem.*, 1989, 359, 1.

208. M.G. Jacko and S.J.W. Price, *Can. J. Chem.*, 1963, **41**, 1560.

209. D.C. Prevorsek, *J. Phys. Chem.*, 1962, **66**, 769.

210. J. Barker, M. Jones and M. Kilner, *Org. Mass Spectrom.*, 1985, **20**, 619.

211. N.W. Alcock, J. Barker and M. Kilner, *Acta Cryst.*, 1988, **C44**, 712.

212. Y. Kai, N. Yasuka, N. Kasai and M. Kakudo, *J. Organomet. Chem.*, 1971, **32**, 165.

213. F. Fischer, R. Gräf and J. Weidlein, *J. Organomet. Chem.*, 1978, **144**, 95.

214. B. Beagley, D.G. Schmidling and I.A. Steer, *J. Mol. Struct.*, 1974, **21**, 437.

215. L.M. Goubinskaya, A.V. Golubinskii, V.S. Mastryukov, L.V. Vilkov and V.I. Bregadse, *J. Organomet. Chem.*, 1976, **117**, C4.

216. Y.Hosokawa, M. Kuroko, T. Aida and S. Inoue, *Macromolecules*, 1991, **24**, 824.

217. G.H. Robinson, W.E. Hunter, S.G. Bott and J.L. Atwood, *J. Organomet. Chem.*, 1987, **326**, 9.

218. B. Lee, W.T. Pennington, G.H. Robinson and R.D. Rogers, *J. Organomet. Chem.*, 1990, **396**, 269.

219. B. Lee, W.T. Pennington and G.H. Robinson, *Organometallics*, 1990, **9**, 1709.

220. G.H. Robinson, W.T. Pennington, B. Lee, M.F. Self and D.C. Hrncir, *Inorg. Chem.*, 1991, **30**, 809.

221. V.L. Goedken, H. Ito and T. Ito, *J. Chem. Soc., Chem. Commun.*, 1984, 1453.

222. V.L. Goedken, J.J. Pluth, S.M. Peng and B. Bursten, *J. Am. Chem. Soc.*, 1976, **98**, 8014.

223. M.C. Weiss, B. Bursten, S.M. Peng and V.L. Goedken, *J. Am. Chem. Soc.*, 1976, **98**, 8021.

224. F.A. Cotton and J. Czuchajowska, Polyhedron, 1990, **9**, 2553.

225. J.L. Hoard, *Science*, 1971, **174**, 1295.

226. V.L. Goedken and M.C. Weiss, *Inorg. Synth.*, 1980, **20**, 115.

227. D.F. Rendle, A. Storr and J. Trotter, *Can. J. Chem.*, 1975, **53**, 2944.

228. M. Veith, O. Recktenwald, *J. Organomet. Chem.*, 1984, **264**, 19.

229. M.A. Khan, C. Peppe and D.G. Tuck, *J. Organomet. Chem.*, 1985, **280**, 17.

230. P. Naumann, W. Strauss and W. Tyrra, *J. Organomet. Chem.*, 1991, **407**, 1.

231. T. Maeda, G. Yoshida, R. Okawara, *J. Organomet. Chem.*, 1972, **44**, 237.

232. M.J.S. Gynane, L.G. Waterworth and I.J. Worrall, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 543.

233. J.D. Forrester, A. Zalkin and D.H. Templeton, *Inorg. Chem.*, 1964, **3**, 63.

234. M.A. Khan, C. Peppe and D.G. Tuck, *Can. J. Chem.*, 1984, **62**, 601.

235. M.F. D'Amato, *Bull. Soc. Chim. Fr.*, 1967, 4026.

236. A.K. Holliday and G.N. Jessop, *J. Chem. Soc. (A)*, 1967, 889.

237. M. Boleslawski, S. Pasynkiewicz and K. Jaworski, *J. Organomet. Chem.*, 1971, **30**, 199.

238. G. Singh, *Organomet. Chem.*, 1975, **99**, 251.

239. T.N. Mitchell, J. Gmehling and F. Huber, *J. Chem. Soc., Dalton Trans.*, 1978, 960.

240. M. Boleslawski, S. Pasynkiewicz and H. Pszonka, *J. Organomet. Chem.*, **28**, C31.

241. M. Boleslawski, S. Pasynkiewicz and M. Harasimowicz, *J. Organomet. Chem.*, 1974, **78**, 61.

242. G.D. Shier and R.S. Drago, *J. Organomet. Chem.*, 1964, **1**, 297.

243. Y. Kawasaki, *J. Organomet. Chem.*, 1967, **9**, 549.

244. R.J.H. Clark, A.G. Davies and R.J. Puddephatt, *J. Am. Chem. Soc.*, 1968, **90**, 6923.

245. E. Amberger and R. Honigschmid-Grossich, *Chem. Ber.*, 1965, **98**, 3795.

246. J. Weidlein, *J. Organomet.* Chem., 1969, **17**, 213.

247. H.D. Hausen, K. Mertz, E. Veigel and J. Weidlein, *Z. Anorg. Allg. Chem.*, 1974, **410**, 156.

248. G.M. Sheldrick, SHELXTL PLUS Service Manual, Nicolet XRD Corp., 1983, Madison, Wisconsin.

249. International Tables for X-Ray Crystallography, Volume IV, Kynoch Press, 1974, Birmingham.

250. B.H. Beggs and R.D. Spencer, *Anal. Chem.*, 1962, **34**, 1590.

251. I. Crossland and F.S. Grevil, *Acta. Chem. Scand.* 1981, Ser. B. **35**, 605.